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# THE PHYSICAL REVIEW

*A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS*

CONDUCTED
WITH THE CO-OPERATION OF THE

## AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS
ERNEST MERRITT, and FREDERICK BEDELL

## CLII

NOVEMBER, 1908

Equilibria in Standard Cells. G. A. HULETT 337
Studies in Luminescence. X. The Phenomena of Phosphorescence considered from the Standpoint of the Dissociation Theory. EDWARD L. NICHOLS and ERNEST MERRITT 367
On the Charges Gained by Insulated Metallic Conductors Surrounded by other Conductors and the Relation of these Charges to the Volta Effect. J. K. ROBERTSON 400
An Investigation of the Electric Intensities and Electric Displacement Produced in Insulators by their Motion in a Magnetic Field. S. J. BARNETT 425

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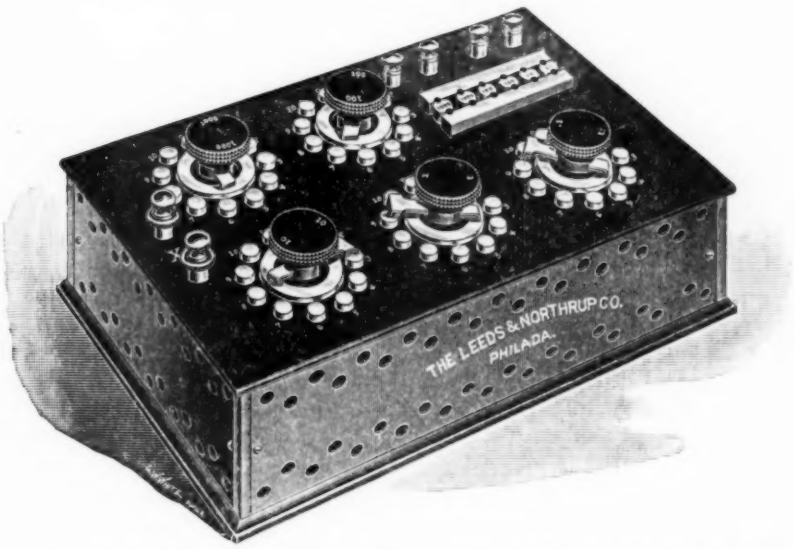


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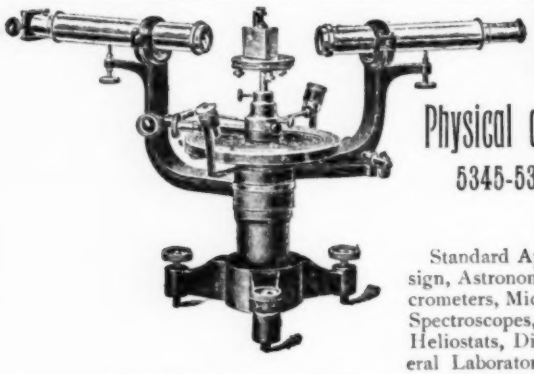

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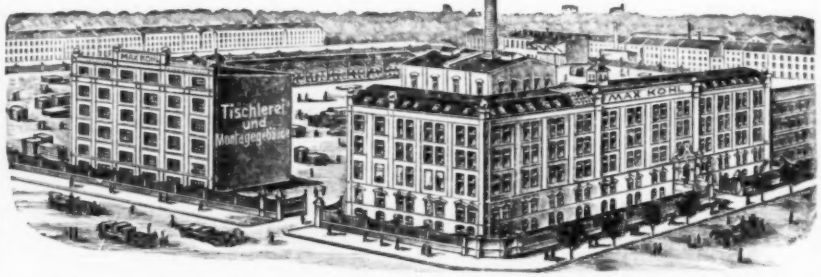


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*Volume XXVII.* *November, 1908.* *Number 5*

THE

# PHYSICAL REVIEW.

## EQUILIBRIA IN STANDARD CELLS.

By G. A. Hulett.

THE two combinations which have shown the greatest reproducibility and constancy are the Clark cell and the Weston or cadmium cell and these cells are very similar in construction:

| | | | | |
|---|---|---|---|---|
| Zinc amalgam | $ZnSO_4\ 7H_2O$ | $Hg_2SO_4$ | $H_2O$ | mercury |
| Cadmium amalgam | $CdSO_4\ \frac{8}{3}H_2O$ | $Hg_2SO_4$ | $H_2O$ | mercury |

Many other combinations have been suggested and tried but have been found wanting in constancy or reproducibility. It has been the universal experience that a metal in the solid state gives an inconstant potential against a solution even of its own salt and, while the cause of this is not fully understood, the fact has restricted the choice of materials to liquid electrodes for standard cells, thus mercury forms one electrode and a liquid amalgam the other. For this amalgam it is desirable that the base metal be well toward the positive end of the electrochemical series and hence far removed from mercury, and that it have a fair solubility in mercury. Gouy[1] gives as the percentage solubility of metals in mercury: Cadmium 4, zinc 1.8, lead 1.3, bismuth 1.2, tin .6, gold .13, and distinctly less for other metals. It is further desirable that the base metal exist in only one state of oxidation and that its salts be well defined. In these requirements zinc and cadmium are distinctly superior to all other metals and it is improbable that other metals will be found to be of service in standard cells. Furthermore the depolarizer must have a certain solubility since mercury shows a constant potential

[1] J. de Physique, 4, 320.

only in electrolytes which contain definite amounts of mercury in solution and experience has shown that this solubility must not be too small, as in the case of the calomel cell, or too great as in the case of the Daniell cell where the depolarizer, copper sulphate, is quite soluble.

Since mercury is the cathode the depolarizer must be a mercur*ous* salt with a solubility of a few parts in a thousand and there are very few available salts of mercury answering to these requirements; mercurous sulphate is distinctly the best, although mercurous chlorate deserves to be considered. It is also to be noted that the acid radical of the base metal must be the same as that of the depolarizer and if mercurous sulphate is used as depolarizer, zinc or cadmium sulphate must be used in the construction of the cell. There are then excellent reasons for devoting attention to the Clark and cadmium cells rather than seeking for other combinations.

*The Cathode Systems.* — The potential difference between an amalgam and an electrolyte varies with the concentration of the metal in the amalgam and so this concentration must be fixed and reproducible for any given temperature. This requirement is attained by utilizing a saturated solution of the metal with an excess of the solid so that at each temperature the proper concentration is automatically produced whether the electrode has lost or gained metal from the electrolyte or in other ways. In the Clark cell this two-phase system is made up of zinc and a saturated amalgam, while in the cadmium cell the solid phase in the amalgam is an isomorphous mixture of mercury and cadmium which has a definite composition for each temperature as well as the liquid amalgam in equilibrium with it. The liquid phase of this cadmium amalgam at 25° has been carefully analyzed and found to contain 5.903 g. of cadmium to 100 g. of mercury and it is probably one of the most accurately reproducible concentrations known. In some experiments on the E.M.F. of cadmium amalgams observations were made on two amalgams containing 10 per cent. and 7 per cent. of cadmium; these formed two-phase systems with different amounts of the solid, and were used as electrodes in a cadmium sulphate solution. The system was made free from oxygen and hermetically sealed in a glass cell; the observations extended over a period of six months, and

although the system was subjected to wide variations of temperature whenever it was brought to 25°, equilibrium was soon established and there never was an E.M.F. between the amalgams greater than .0000012 volt; it was generally less than this, but if this difference was all due to differences in the concentration of cadmium in the two liquid phases it indicated differences of only seven parts in a million. In order that this two-phase amalgam may give a definite potential difference, it is necessary that it be in contact with a solution which contains a cadmium salt of definite concentration, and here again use is made of the property of a saturated solution with an excess of the solid salt. Crystallized cadmium sulphate, $CdSO_4 \frac{8}{3}H_2O$, is a particularly well-defined salt and gives a concentration of 3.363 mols in a liter at 25°, the density of this solution is 1.6176.

Since the anode is made up of two metals, cadmium and mercury, it is essential for equilibrium that the electrolyte contain in solution salts of both metals and that there be a definite ratio between the concentrations of these salts, depending on the relative concentration of the metals in the electrode and upon their relative solution pressures or positions in the electrochemical series. The most thoroughly investigated case of this kind is the equilibrium between mercury, silver and a solution of their nitrates.[1] It was shown that silver did not completely remove mercury from solution and that mercury, when brought into contact with a silver nitrate solution, did go into solution and reduce an equivalent amount of silver. From whichever side approached there resulted a definite equilibrium with both silver and mercury in the metal phase and in the solution, the equilibrium was represented by the following relation proposed by Nernst[2] $\sqrt[n_1]{P_1/p_1} = \sqrt[n_2]{P_2/p_2}$, where $P_1$, $P_2$ represent the solution pressures of the two metals and $p_1$, $p_2$ the osmotic pressures of the ions of these metals in the electrolye; $n_1$ and $n_2$ represent their respective valencies. It was further pointed out by Reinders that in case the metals formed a solution (liquid or solid) that $P_1$ and $P_2$ would vary with their respective concentrations in the metal phase and the equation was correspondingly modified.

[1] Ogg, Zeit. Phys. Chem., 27, 285. Reinders, Zeit. Phys. Chem., 54, 609.
[2] Zeit. Phys. Chem., 22, 537.

It must be concluded therefore that cadmium will not completely remove mercury from solution and that if mercury is brought into contact with a cadmium sulphate solution, some of the mercury will go into solution and force out an equivalent amount of cadmium. Reinders [1] suggested that this state of affairs existed in the standard cells, but due to the wide difference between cadmium and mercury in the electrochemical series, the equilibrium concentration of mercury in the anode leg must be very small. Observations on the cells themselves tend to confirm this point since the anode shows its correct potential difference soon after a cell is constructed, later mercurous sulphate diffuses over from the cathode and then there is a certain concentration of mercury about the amalgam, but the arrival of the dissolved mercury at the anode is not accompanied by a change in E.M.F., so it would seem that the equilibrium concentration of mercury about the anode was already present before the mercury diffused over from the cathode, having been furnished by the interaction of the amalgam and the solution. Some results on the E.M.F. of dilute amalgams, which will soon be published, give more direct evidence of this relation and indicate that the mercury concentration is very small. It is to be remembered, however, that it is not the absolute but the relative concentrations which are of importance in determining electromotive forces.

The anode of a standard cell may then be made up of an electrode in two phases, the liquid amalgam has an exceedingly exact and reproducible concentration for each temperature and when this equilibrium is established the solid phase has of course the same potential as the liquid phase and does not show the irregularities exhibited by a solid metal electrode. The electrolyte about this electrode is saturated with cadmium sulphate and an excess of the crystals insures a definite concentration of cadmium in the electrolyte for each temperature while the interaction of the amalgam and this solution furnishes an equally definite mercury concentration in the liquid surrounding the electrode. The anode system is thus seen to be made up of five phases: solid and liquid amalgam, solution, solid salt of the base metal, and vapor. The components are therefore: mercury, base metal, water and acid radical and thus for each temperature they form a non-variant system.

[1] Zeit. Phys. Chem., 42, 232.

It is evident that the equilibria in these anode systems are rapidly established as soon as the temperature is fixed. Of the two anode systems it is probable that they are equally reproducible and constant, the solubility of zinc sulphate crystals changes very greatly with the temperature and there is a tendency for these crystals to "cake" above the amalgam, while the cadmium sulphate crystals have an exceptionally small temperature-solubility coefficient and have not shown this tendency. The tendency of the zinc amalgam to cause the platinum contact wire to crack the glass has been a source of trouble with Clark cells, also the zinc amalgam slowly generates hydrogen from its sulphate solution so it is probable that a zinc sulphate solution has a fair concentration of hydrogen ions while there is no evidence of the liberation of hydrogen in the anode system of the cadmium cell and it is probable from other experiments also that a cadmium sulphate solution is only slightly hydrolyzed, if at all, and so contains practically no hydrogen ions. The cadmium anode is more completely reversible than the zinc anode, for in as far as hydrogen is liberated with the deposition of the metal the change is not reversible, but this does not effect the equilibrium, reproducibility or constancy of the zinc anode system and while the lack of hydrogen ions in the cadmium sulphate solution is an advantage in the anode system of the cadmium cell, it is the cause of a state of unstable equilibrium in the cathode system of this cell as the following results show. In this respect the acid qualities of the zinc sulphate solution constitute a very decided advantage.

Reinders[1] was the first to point out that these cells could not be considered as one system since the electrolyte at the cathode is saturated with mercurous sulphate which continually diffuses over to the anode and is there reduced to a very small concentration by the amalgam. Equilibrium would be established only on the disappearance of the base metal from the anode or the disappearance of the mercurous sulphate as a solid phase, in either case the E.M.F. would become zero or inconstant. This type of cell is made up of two distinct systems which are in electrolytic contact but not in equilibrium with each other, but as the cells are constructed the diffusion from cathode to anode is so slow that the life

[1] Konink. Akad. Wetensch. Amsterdam, Versl. 11, 115.

of the combination is very great. It was further noted by Reinders that, for a constant and reproducible E.M.F., it was essential that both the anode system and the cathode system be nonvariant systems when the temperature was fixed. The Clark cell conforms to these requirements but the results now at hand show that the cathode system of the cadmium cell does not.

*The Cathode Systems.* — The materials used in constructing the cathode system of the cadmium cell are: Mercury, mercurous sulphate, cadmium sulphate and water. An excess of the two sulphates are used and it may be assumed that there results a solution saturated in respect to $CdSO_4 \frac{8}{3}H_2O$ and $Hg_2SO_4$, provided that these salts are in their stable forms at the temperatures considered, do not form isomorphous mixtures, double salts or interact chemically. The mercury will not be pure but will contain a small equilibrium concentration of cadmium due to its interaction with the solution. There appears then a potential difference between this electrode and the solution which is a function only of the temperature and if the premises are correct it may be concluded that rotating this system will not affect the potential difference provided the materials are not reduced to such a fine state of subdivision that the effect due to surface tension becomes measurable. But it has been found[1] that there was a very decided change in the potential difference when this cathode system of the cadmium cell was rotated, a slow increase was observed amounting in some cases to two millivolts. The apparatus used in rotating the system gave a thorough mixing of the contents but avoided grinding the solids to a fine powder or reducing the mercury to small globules. Indirect evidence was also obtained to show that the observed change in potential difference was in no way due to surface tension. It seemed possible that the dissolved oxygen had changed some of the mercurous sulphate to the more soluble mercuric form and that the resulting increased mercury concentration caused the increased potential difference. This obvious explanation was rigidly tested[2] but it was found that the absence of oxygen made no difference in the results of the rotation experiment and considerable indirect evidence also pointed to the

[1] PHYS. REV., 23, 176, and 25, 16.
[2] PHYS. REV., 25, 19–24.

same conclusion. The evidence on this point seemed so decisive that it is to be concluded that dissolved oxygen plays no rôle whatever in these systems. If the *rate* of solution of mercurous sulphate was slow the equilibrium point would be slowly approached and only on rotating the system, but it has been frequently noticed that the cell assumes a certain E.M.F. soon after it is constructed and if its value undergoes any change it is to decrease, while an increasing mercury concentration would mean an increasing E.M.F. This fact seems to effectively dispose of the idea of a slow rate of solution of the mercurous sulphate in a cadmium sulphate solution; it shows that, at least the layer next to the mercury electrode, dissolved as much mercury sulphate as it will in a very short time.

There was still the possibility that the mercurous sulphate was hydrolyzed by the cadmium sulphate solution with the formation of a basic salt and an acid solution, a reaction which would proceed until a certain acid concentration was established. This point was tested by adding acid to the system and it was found that it did not then show the slowly increasing potential difference but came to a constant value very soon after the rotation was begun. This was good evidence that mercurous sulphate, conforming to its well known tendency, did hydrolyze in a cadmium sulphate solution. The only evidence for the increase in the mercury concentration was the increase in the potential difference observed in the rotation experiments. This increase of some two millivolts would indicate, according to Nernst logarithmic relation, an increase of some 15 per cent. in the concentration of the mercurous sulphate, assuming that there was a gram of mercurous sulphate in a liter of the solution and it was largely dissociated; but if it was only slightly dissociated in the cadmium sulphate solution, the observed change in potential difference would indicate a much greater increase in the mercury concentration and it therefore seemed possible to detect analytically such changes in concentration if they existed.

The clear solution from the cathode system had a density of 1.6176, contained 760 g. of $CdSO_4$ in a liter but only about one gram of mercurous sulphate and considerable difficulty was encountered until a special method of analysis was devised. It was found that an excess of hydrochloric acid entirely prevented the precipita-

tion of CdS by sulphuretted hydrogen but all the mercury was thrown out as a black sulphide. However the difficulty of separating this sulphide of mercury from the viscous liquid was so great that it could not be used for quantitative determinations although it served as a method of detecting traces of mercury in the concentrated cadmium sulphate solution and also to estimate small quantities colorimetrically. Hydrochloric acid was found to precipitate mercury from these solutions as mercurous chloride which Ley and Himbuchsen[1] have shown to have a solubility of only .2 mg. in a liter, much less soluble than silver chloride and it was found that the mercurous chloride soon coagulated and filtered nicely. It is known however that these solutions also contain a certain very small concentration of mercur*ic* mercury, since there is always an equilibrium established between the mercur*ous* and mercur*ic* mercury in a solution which is in contact with mercury, but in the case of mercury this equilibrium favors the *-ous* state of oxidation so that probably less than one per cent. of the mercury in solution was in the *-ic* state. In consideration of this point it was deemed best to follow the precipitating reagent, HCl, with a reducing agent and sulphur dioxide was used. These reagents so completely removed the mercury that sulphuretted hydrogen failed to show a trace of mercury in the filtrate. The mercurous chloride was easily collected in a Gooch crucible, washed with water and dried in a vacuum desiccator over calcium chloride.[2] It had been previously shown that this precipitate could be completely dried in this way without loss while it was noticeably volatile at 100° and again it has been found that this is a most satisfactory analysis and an exceedingly exact method of determining mercury.

As soon as it was found possible to determine the mercury quantitatively in these cathode solutions the rotation experiments were repeated and a complete analysis was made of the clear solutions together with the density, conductivity and potential difference against mercury. These determinations have been made also on systems to which known amounts of sulphuric acid were added and from these results the solubility curve of mercurous sulphate as a

[1] Zeit. f. Electrochem., 10, 301.
[2] Zeit. Phys. Chem., 49, 500.

function of the sulphuric acid concentration in this system has been determined and the curve gives definite information about the hydrolysis of mercurous sulphate in a cadmium sulphate solution.

*Materials, Apparatus and Method.* — In the previous experiments[1] it was found that either the electrolytic mercurous sulphate or the chemically prepared salt gave high values in the rotated cathode system of the cadmium cell. The essentials are that the depolarizer be normal mercurous sulphate, that acid be rigidly excluded from the system and that the system be closed during the rotation. For the present work the mercurous sulphate was prepared by adding, drop by drop, a molecular solution of mercurous nitrate to a rapidly stirred sulphuric acid solution. Two liters of this acid, density 1.15, were used in preparing 125 grams of the mercurous sulphate. The stirring was done with a motor and three hours were taken for the precipitation so as to obtain a well crystallized product free of inclusions. The action of light was avoided while with the excess of acid used and metallic mercury in both solutions, the basic salts could not have formed. The product was pure white, distinctly crystalline and easily washed, but as the complete removal of acid was important particular attention was given to this operation. The salt was first thoroughly washed with molecular sulphuric acid, then with absolute alcohol and finally with some of the solution in which it was to be used, this was done in a Gooch crucible with filter disk and strong suction was used after each washing. Cells have been constructed from time to time with this preparation and they have shown the normal value and have remained constant. The cadmium sulphate was recrystallized and only the clear well rinsed crystals used, as this salt is not isomorphous with other sulphates impurities were not feared. The zinc sulphate was more troublesome to obtain in a satisfactory state. Iron, lead and cadmium were removed by the method of Mylius and Fromm.[2] The salt was then recrystallized and the crystals centrifuged (Richards). The mercury used was chemically purified with an acid solution of mercurous nitrate and then distilled under diminished pressure with a current of air passing through with the vapor,[3] a method that insures the removal of such metals as zinc and cadmium.

[1] PHYS. REV., 23, 177, and 25, 19.
[2] Zeit. anorg. Chem., 9, 144.
[3] PHYS. REV., 21, 388.

Conductivity water was used where justified in making the solutions, and when acid was to be added to the system the zinc or cadmium sulphates were dissolved in sulphuric acid of known strength. These acids were all made by dilution from the original molecular sulphuric acid which was made from distilled sulphuric acid and conductivity water, the density of this solution was 1.05948 at 25° and it was found to be 1.012 molar by comparison with a carefully analyzed hydrochloric acid solution.

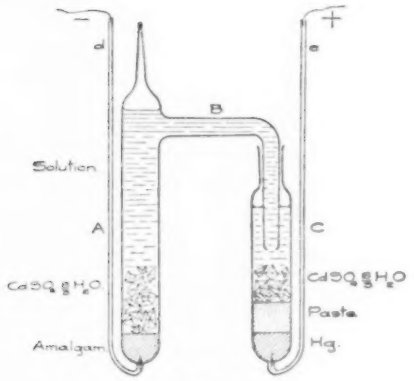


Fig. 1.

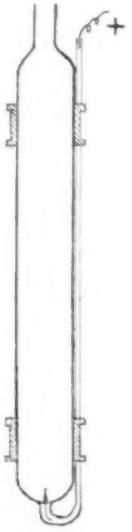


Fig. 2.

The systems were brought to equilibrium in tubes 32 mm. in diameter and 150 mm. long, made as shown in Fig. 2. A tube was charged with about 100 g. of mercury, a good excess, then with about 20 g. of the crushed zinc or cadmium sulphate crystals and 25 g. of the properly washed mercurous sulphate crystals. Finally the tube was filled to the neck with the saturated zinc or cadmium sulphate solution. Attention was given to really saturating these solutions at about 25°. The tube was now closed with a cork and a rubber cap was drawn over the cork and neck of the tube to securely close the system. The tube was rotated in the bath in a horizontal position and about the longer axis. It rested in the loops of little belts which extended down from a shaft which

was fixed above the bath and its speed so regulated that the tube rotated at a rate of 10 revolutions per minute. This rate gave a most thorough mixing of the contents of the tube, but was not rapid enough to grind the solid contents to a powder or to cause the mercury to become divided into fine globules. From time to time the tube was brought to an upright position in the bath, the cap and cork were removed and the anode of the adjustable cell *A*, Fig. 1, was brought into contact with the contents of the tube and thus the E.M.F. between the amalgam of this anode and the mercury of the system was determined. Whatever changes in the E.M.F. were observed between successive observations were known to be due to changes in the potential difference of the rotated cathode system because the anode was not rotated, and with its own unrotated cathode *C*, Fig. 1, there was always a check on the constancy of the anode and also a comparison of the rotated and unrotated system since the same materials served for the construction of both of these systems. Each equilibrium tube was rotated until the potential difference of the system became constant and in some cases this required two weeks or more. It is to be noted that during the rotation nothing could enter or leave the system nor at any time since the system was quiet when the anode was adjusted and a diffusion of dissolved mercury out through the narrow tube *B* of the anode tester during the time of making a measurement was not to be considered.[1]

When the system was in equilibrium, as indicated by no further increase in the E.M.F., the tube was allowed to stand quietly in the bath for a day, or until the liquid was perfectly clear, and then it was drawn up into a large pyknometer through a little glass tube. The pyknometer and contents were brought to 25° and the mass of a known volume of the solution was determined. This solution

[1] Attention is called to this point since it will be readily seen that if the anode and cathode systems had been in liquid contact during the rotation that the diffusion of mercurous sulphate to the anode, aided by convection, would have been a maximum, and since the hydrolysis of mercurous sulphate in this system is an exceptionally slow reaction there would have been little increase in the mercury concentration in the cathode system; such methods would not show the real changes that did take place. Neglect to guard against this point may possibly account for the low results obtained in some of the experiments lately made by Drs. F. A. Wolff and C. E. Waters. Bull. Bureau of Standards, Vol. 4, 81.

was transferred, with a little water, to a flask and made acid with sulphuric acid and then the mercury was precipitated with 5 c.c. of strong hydrochloric acid and finally sulphur dioxide was bubbled into the solution to reduce the small amount of mercuric mercury. The HgCl coagulated nicely and required only a very thin felt in the Gooch crucible, it was determined as already described (p. 109) and the weight calculated to $Hg_2SO_4$. The results are regarded as reliable to .1 mg. The clear filtrate was evaporated in a platinum dish, heated to expel the hydrochloric acid and excess of sulphuric acid and, after cooling in a desiccator, weighed. The dish and sulphate was then reheated for an hour at about 500° in an atmosphere containing a little $SO_3$ vapor, cooled and reweighed.

Thus for each system the mass of the solution, of the $CdSO_4$, and the mercury as HgCl were directly determined while the water was had by difference. In case acid had been added a further calculation was necessary; for example in Experiment No. 1, "cadmium system in molar sulphuric acid," the dissolved $CdSO_4 \frac{8}{3}H_2O$ added its water of crystallization to the solution, but the amount was obtained from the weight of the $CdSO_4$ and with this allowance the amount of $H_2SO_4$ in the volume of the solution taken was determinable; in this experiment, where molar sulphuric acid had been used, the solution was only .810 molar in respect to sulphuric acid.

The thermostat used in the previous work [1] maintained the temperature to within .02 of 25° throughout the long runs and materially aided in the accuracy of many of the measurements. The temperature was determined by a 1/50° calibrated thermometer which was checked at 32.383°, the transition point of sodium sulphate (Richards and Wells). The two pyknometers used were calibrated from time to time and it was found that the mass of the pyknometer, alone or filled with water, was determinable to less than .5 mg. The volumes were, No. 1 47.7605 and No. 2 49.0856 cm. at 25°. All weighings were made by substitution of calibrated weights and, where justifiable, vacuum corrections were made. The conductivity measurements were made in the usual way, a long narrow Arrhenius form of cell with a capacity factor of 8,040 was used.

[1] Phys. Rev., 25, 19.

In the E.M.F. determinations the same apparatus and precautions were used as in the previous work;[1] it was found quite necessary to thoroughly insulate the lead wires to the rotation tubes and for the adjustable cells since they dipped into the water-bath. This was done by covering them with glass tubes as indicated in Figs. 1 and 2.

### *Cathode Systems of the Cadmium Cell.*

*Experiment 1.* — System in 1.012 molar sulphuric acid, rotated 8 days, 25°.

| | | | | | Moles in a Liter. |
|---|---|---|---|---|---|
| Mass of solution | in 49.0856 | c.c. | 75.377 | g. | |
| " $CdSO_4$ | " 49.0856 | " | 27.384 | " | 2.6757 |
| " $Hg_2SO_4$ | " 49.0856 | " | .0371 | " | .001524 |
| " $H_2O$ | " 49.0856 | " | 44.051 | " | 48.683 |
| " $H_2SO_4$ | " 49.0856 | " | 3.905 | " | .810 |
| $D_{25}$ | 1.53564 | | | E.M.F | 1.01678 *V.* |
| $\lambda_{25}$ | .14423 | | | Adjustable cell | 1.01671 " |

*Experiment 2.* — System in .506 molar sulphuric acid, rotated 5 days, 25°.

| | | | | | Moles in a Liter. |
|---|---|---|---|---|---|
| Mass of solution | in 47.7605 | c.c. | 75.209 | g. | |
| " $CdSO_4$ | " 47.7605 | " | 29.989 | " | 3.0116 |
| " $Hg_2SO_4$ | " 47.7605 | " | .0442 | " | .001867 |
| " $H_2O$ | " 47.7605 | " | 43.330 | " | 50.860 |
| " $H_2SO_4$ | " 47.7605 | " | 1.847 | " | .384 |
| $D_{25}$ | 1.57511 | | | E.M.F | 1.01747 *V.* |
| $\lambda_{25}$ | .07738 | | | Adjustable cell | 1.01745 " |

*Experiment 3.* — System in .2024 molar sulphuric acid, rotated 6 days, 25°.

| | | | | | Moles in a Liter. |
|---|---|---|---|---|---|
| Mass of solution | in 47.7605 | c.c. | 76.433 | g. | |
| " $CdSO_4$ | " 47.7605 | " | 32.0905 | " | 3.2226 |
| " $Hg_2SO_4$ | " 47.7605 | " | .0478 | " | .002017 |
| " $H_2O$ | " 47.7605 | " | 43.570 | " | 50.641 |
| " $H_2SO_4$ | " 47.7605 | " | .7263 | " | .155 |
| $D_{25}$ | 1.60032 | | | E.M.F | 1.01808 *V.* |
| $\lambda_{25}$ | .05350 | | | Adjustable cell | 1.01802 " |

*Experiment 4.* — System in .1012 molar sulphuric acid, rotated 10 days, 25°.

[1] PHYS. REV., 25, 29.

| | | | | | Moles in a Liter. |
|---|---|---|---|---|---|
| Mass of solution | in 47.7605 | c.c. | 76.836 | g. | |
| " $CdSO_4$ | " 47.7605 | " | 32.805 | " | 3.2944 |
| " $Hg_2SO_4$ | " 47.7605 | " | .04937 | " | .002084 |
| " $H_2O$ | " 47.7605 | " | 43.622 | " | 50.700 |
| " $H_2SO_4$ | " 47.7605 | " | .360 | " | .0769 |
| $D_{25}$ | 1.60880 | | | E.M.F. | 1.01823 *V.* |
| $\lambda_{25}$ | .04674 | | | Adjustable cell | 1.01821 " |

*Experiment 5.* — System in .05064 molar sulphuric acid, rotated 7 days, 25°.

| | | | | | Moles in a Liter. |
|---|---|---|---|---|---|
| Mass of solution | in 47.7605 | c.c. | 77.032 | g. | |
| " $CdSO_4$ | " 47.7605 | " | 33.120 | " | 3.3260 |
| " $Hg_2SO_4$ | " 47.7605 | " | .05176 | " | .002185 |
| " $H_2O$ | " 47.7605 | " | 43.680 | " | 50.722 |
| " $H_2SO_4$ | " 47.7605 | " | .180 | " | .0384 |
| $D_{25}$ | 1.61289 | | | E.M.F. | 1.01834 |
| $\lambda_{25}$ | .04372 | | | Adjustable cell | 1.01834 |

*Experiment 6.* — System in .02024 molar sulphuric acid, rotated 13 days, 25°.

| | | | | | Moles in a Liter. |
|---|---|---|---|---|---|
| Mass of solution | in 49.0856 | c.c. | 79.304 | g. | |
| " $CdSO_4$ | " 49.0856 | " | 34.262 | " | 3.348 |
| " $Hg_2SO_4$ | " 49.0856 | " | .05514 | " | .002265 |
| " $H_2O$ | " 49.0856 | " | 44.914 | " | 50.910 |
| " $H_2SO_4$ | " 49.0856 | " | .0737 | " | .0153 |
| $D_{25}$ | 1.61565 | | | E.M.F. | 1.01847 *V.* |
| $\lambda_{25}$ | .04180 | | | Adjustable cell | 1.01835 " |

*Experiment 7.* — System without acid added, rotated 21 days, 25°.

| | | | | | Moles in Liter. |
|---|---|---|---|---|---|
| Mass of solution | in 47.7605 | c.c. | 77.251 | g. | |
| " $CdSO_4$ | " 47.7605 | " | 33.470 | " | 3.361 |
| " $Hg_2SO_4$ | " 47.7605 | " | .0640 | " | .002701 |
| " $H_2O$ | " 47.7605 | " | 43.717 | " | 50.800 |
| $D_{25}$ | 1.61747 | | | E.M.F. | 1.01905 *V.* |
| $\lambda_{15}$ | .04037 | | | Adjustable cell | 1.01837 " |

*Experiment 8.* — System without acid added, rotated 21 days, 25°.

| | | | | | Moles in Liter. |
|---|---|---|---|---|---|
| Mass of solution | in 49.0856 | c.c. | 79.405 | g. | |
| " $CdSO_4$ | " 49.0856 | " | 34.435 | " | 3.365 |
| " $Hg_2SO_4$ | " 49.0856 | " | .0726 | " | .002980 |
| " $H_2O$ | " 49.0856 | " | 44.897 | " | 50.770 |
| $D_{25}$ | 1.61771 | | | E.M.F. | 1.01940 *V.* |
| $\lambda_{25}$ | .04057 | | | Adjustable cell | 1.01836 " |

*Experiment 9.* — System without acid added. Fresh solution was added to the solids of experiment 8, rotated 20 days, 25°.

| | | | | | |
|---|---|---|---|---|---|
| Mass of solution in | 49.0856 | c.c. | 79.402 | g. | Moles in a Liter. |
| " $CdSO_4$ " | 49.0856 | " | 34.417 | " | 3.363 |
| " $Hg_2SO_4$ " | 49.0856 | " | .0742 | " | .003047 |
| " $H_2O$ " | 49.0856 | " | 44.911 | " | 50.790 |
| $D_{25}$ | 1.01765 | | | | E.M.F. 1.02015 *V.* |
| $\lambda_{25}$ | .04061 | | | | Adjustable cell 1.01836 " |

*Cathode Systems of the Clark Cells.*

*Experiment 10.* — System with 1.012 molar sulphuric acid, rotated 8 days, 25°.

| | | | | | |
|---|---|---|---|---|---|
| Mass of solution in | 49.0856 | c.c. | 72.2942 | g. | Moles in a Liter. |
| " $ZnSO_4$ " | 49.0856 | " | 24.000 | " | 3.028 |
| " $Hg_2SO_4$ " | 49.0856 | " | .0296 | " | .001216 |
| " $H_2O$ " | 49.0856 | " | 45.500 | " | 51.460 |
| " $H_2SO_4$ " | 49.0856 | " | 2.765 | " | .5744 |
| $D_{25}$ | 1.47436 | | | | E.M.F. 1.41588 *V.* |
| $\lambda_{25}$ | .08588 | | | | Adjustable cell 1.41595 " |

*Experiment 11.* — System with .506 molar sulphuric acid, rotated 3 days, 25°.

| | | | | | |
|---|---|---|---|---|---|
| Mass of solution in | 49.0856 | c.c. | 72.7524 | g. | Moles in a Liter. |
| " $ZnSO_4$ " | 49.0856 | " | 25.355 | " | 3.1993 |
| " $Hg_2SO_4$ " | 49.0856 | " | .03516 | " | .001444 |
| " $H_2O$ " | 49.0856 | " | 46.032 | " | 52.060 |
| " $H_2SO_4$ " | 49.0856 | " | 1.330 | " | .270 |
| $D_{25}$ | 1.48214 | | | | E.M.F. 1.41813 *V.* |
| $\lambda_{25}$ | .06110 | | | | Adjustable cell 1.41810 " |

*Experiment 12.* — System with .1012 molar sulphuric acid, rotated 3 days, 25°.

| | | | | | |
|---|---|---|---|---|---|
| Mass of solution in | 49.0856 | " | 73.155 | g. | Moles in a Liter. |
| " $ZnSO_4$ " | 49.0856 | " | 26.402 | " | 3.331 |
| " $Hg_2SO_4$ " | 49.0856 | " | .03942 | " | .001619 |
| " $H_2O$ " | 49.0856 | " | 46.455 | " | 52.537 |
| " $H_2SO_4$ " | 49.0856 | " | .259 | " | .0537 |
| $D_{25}$ | 1.49037 | | | | E.M.F. 1.42016 *V.* |
| $\lambda_{25}$ | .04500 | | | | Adjustable cell 1.42015 " |

*Experimeut 13.*—System without acid added, rotated 5 days, 25°.

| | | | | | |
|---|---|---|---|---|---|
| Mass of solution in | 49.0856 | c.c. | 73.288 | g. | Moles in a Liter. |
| " $ZnSO_4$ " | 49.0856 | " | 26.637 | " | 3.361 |
| " $Hg_2SO_4$ " | 49.0856 | " | .04108 | " | .001687 |
| " $H_2O$ " | 49.0856 | " | 46.610 | " | 52.710 |
| $D_{25}$ | 1.49308 | | | | E.M.F. 1.42047 *V.* |
| $\lambda_{25}$ | .04141 | | | | Adjustable cell 1.42043 " |

In the present state of our knowledge of solutions, solubility results are best expressed as parts or moles to 100 g. of solvent, but in the present case the solvent water was determined by difference and included all the other errors while the volume of the solution analyzed was so accurately known it seemed best to calculate the results to moles in a liter and these data are found in the last column of the tables. The character of the curves obtained were the same whichever way the observations were calculated.

It is well known that acid decreases the E.M.F. of standard cells and this may be seen at once from the tabulated results. On plotting the electromotive forces as a function of the acid concentrations, the curve appeared to be a straight line, and in the case of the Clark cell the most probable curve for the four determinations showed that a change of one millivolt in the E.M.F. of the cell corresponded to a change of .121 mole in a liter of the sulphuric acid. In the case of the cadmium cell the linear function applies only for concentrations greater than .1 molar acid, since for very small acid concentrations the E.M.F. curve changes are very great and follow quite different curves, but for the region of .1 molor sulphuric acid and beyond a change of one millivolt in the E.M.F. of the cell corresponds to a change of .410 mole in the acid concentration of the electrolyte, so sulphuric acid has a much less effect on the E.M.F. of the cadmium cell than in the Clark cell.

On inspecting the tables it is seen that the rotation did not affect the E.M.F. of the Clark cell; in experiment 13 the rotated cathode system of the Clark cell had the same potential difference as did the unrotated cathode system of the adjustable cell. This is also true in experiments 10, 11 and 12 where acid had been added. In the case of the cadmium cell where sufficient acid had been added there was no essential difference between the rotated and unrotated cathode systems, as was found in experiments 1, 2, 3, 4 and 5. But in experiment 6 with only .0153 mole of sulphuric acid to the liter of electrolyte, the rotated system was .00012 volt higher than the unrotated adjustable cell and in experiments 7, 8 and 9 where no acid was added the observed increase in E.M.F. was from .00070 to .00189 volt. These high values did not remain constant when the rotation was stopped but decreased on standing; the first

readings were taken in about one minute after stopping the rotation and then at intervals. On plotting these observations it was possible to get the value at the moment of stopping the rotation. For example in experiment 9 one of the last observations made was as follows:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1½ | minutes | after | stopping | the | rotation | E.M.F. | 1.0200 |
| 2½ | " | " | " | " | " | " | 1.01992 |
| 6½ | " | " | " | " | " | " | 1.01977 |
| 24 | " | " | " | " | " | " | 1.01968 |

and this indicated 1.02015 as the initial value with an error probably not greater than .00005. That this was the true value was shown by removing some of the clear supernatant liquid and testing it on a clean mercury surface.[1] The reason for the decrease will soon be given.

It was expected that sulphuric acid would decrease the solubility

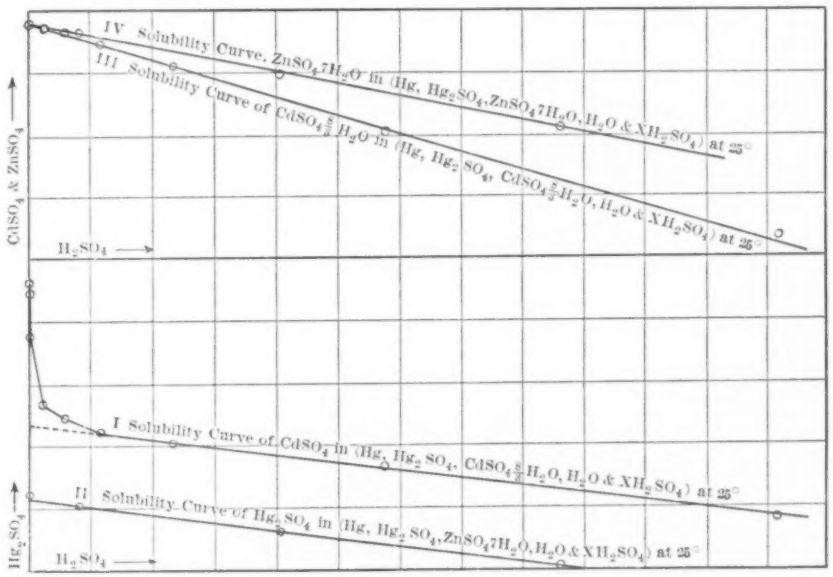
IV Solubility Curve, $ZnSO_4 7H_2O$ in (Hg, $Hg_2SO_4$, $ZnSO_4 7H_2O$, $H_2O$ & $XH_2SO_4$) at 25°
III Solubility Curve of $CdSO_4\frac{5}{3}H_2O$ in (Hg, $Hg_2SO_4$, $CdSO_4\frac{5}{3}H_2O$, $H_2O$ & $XH_2SO_4$) at 25°
$CdSO_4$ & $ZnSO_4$
$H_2SO_4$
I Solubility Curve of $CdSO_4$ in (Hg, $Hg_2SO_4$, $CdSO_4\frac{5}{3}H_2O$, $H_2O$ & $XH_2SO_4$) at 25°
II Solubility Curve of $Hg_2SO_4$ in (Hg, $Hg_2SO_4$, $ZnSO_4 7H_2O$, $H_2O$ & $XH_2SO_4$) at 25°
$Hg_2SO_4$
$H_2SO_4$

Fig. 3.

of the sulphates in these systems and, for a given temperature, the solubility of the mercurous sulphate and cadmium sulphate (or zinc sulphate) should decrease uniformly with increasing acid concentra-

[1] PHYS. REV., 25, 27.

tion. On plotting the results this was found to be true for all *except the mercurous sulphate in the cathode system of the cadmium-cell;* the results are represented by curve *I*, Fig. 3. For a concentration of .810 molar sulphuric acid in the system the mercurous sulphate was .001524 mole in a liter and as the acid concentration decreased the mercury concentration increased uniformly until the acid had been reduced to .08 mole in a liter. The results between these values gave a straight line which has been extended to zero concentration of acid. The mercurous sulphate found for the .0384 molar sulphuric acid was distinctly above this line by 4.5 per cent. of its value, while for the concentration of .0153 acid in the system the mercury was 7.3 per cent. too high and for the systems without acid was some 35 per cent. greater than the normal solubility obtained by exterpolating the curve. In short there is a distinct break in the solubility curve of mercurous sulphate in the cathode system of the cadmium cell as soon as the sulphuric acid concentration has been reduced to .08 mole in a liter, and this indicates a change in the nature of the solid mercurous sulphate or that a chemical reaction begins and takes place below this concentration. From the well known behavior of mercury salts there can be no hesitation in concluding that a saturated solution of cadmium sulphate hydrolyzes mercurous sulphate. It is also evident that this change in the solubility curve of mercurous sulphate cannot be due to the cadmium sulphate since the solubility curve of this salt in the system increased uniformly with decreasing acid concentration without a suggestion of discontinuity at .08 mole of sulphuric acid.

When mercurous sulphate comes into a cadmium sulphate solution it begins to dissolve and to hydrolyze and instead of the mercury concentration in the solution becoming constant when the system is saturated in respect to mercurous sulphate, this concentration keeps on increasing as the slow hydrolysis yields basic salt and acid. In time the solution becomes saturated in respect to this basic salt which then appears as a solid phase. But the hydrolysis will not stop until the acid formed by the reaction has reached the equilibrium concentration of .08 mole in a liter. Now the basic salt has a very small solubility, less than the normal salt which is only .00214 mole in a liter, so the acid concentration is

very far from the equilibrium concentration when the basic salt appears as a solid. This state of affairs at once explains the seemingly abnormal behavior of the cells in which mixtures of basic and normal salts were used as depolarizers.[1] It was expected that any mixture of basic and normal salt which contained an excess of both salts, would give a definite concentration of mercury for each temperature and thus a definite reproducible value to the cells. But they did not agree and all showed a decreasing E.M.F. indicating that the cathode systems were not in equilibrium. The explanation that seemed most probable at that time was as follows: Since the basic salt added to the system had been formed by the action of water on mercurous sulphate, it was possibly not the same as that formed in a cadmium sulphate solution and was therefore ineffective in stopping the hydrolysis. Now it appears that the basic salt was quite incapable of stopping the hydrolysis and since the necessary acid concentration was lacking the behavior of these cells is readily understood. Cox[2] concluded that there is but one basic mercurous sulphate and the behavior of these cells may now be brought into harmony with this view. We may then write the reaction as follows: $2Hg_2SO_4 + 2H_2O = Hg_2(OH)_2Hg_2SO_4 + H_2SO_4$ and it is possible to get some idea of the extent of this hydrolysis in the rotation experiments. In none of these experiments was the maximum mercury concentration, the point of saturation of normal and basic salt, attained so we may conclude that the basic salt formed remained in solution, and the increase in the mercury concentration during the rotation was a measure of the amount of hydrolysis. In experiment 9, the analysis showed .003047 mole of mercurous sulphate in a liter while the normal solubility of mercurous sulphate in a cadmium sulphate solution may be taken to be .00214 mole in a liter, as seen from curve *I*, Fig. 3. The difference, .0009 mole, represents the amount of hydrolysis and, according to the reaction, a mole of mercurous sulphate gives only .5 mole of sulphuric acid on hydrolyzing so the acid concentration in this system was only .00045 mole of sulphuric acid in a liter, an amount that could readily escape detection by any ordinary means and we see at once why the

[1] PHYS. REV., 22, 328.
[2] Zeit. anorg. Chem., 40, 178.

attempts to find acid in the rotated systems or old cells have failed. Attention is called to the small amount of this hydrolysis in a cadmium sulphate solution, even under the most favorable conditions the reaction had only produced .00045 mole of sulphuric acid in three weeks where .08 was required before equilibrium was established. This 0.009 mole in a liter represents the total change in three weeks in the rotated system, but if the reaction was largely at the mercury surface the rate may have been fairly rapid at that point, and there are good reasons for this assumption.

Lord Rayleigh in 1884 suggested that impurities in the mercurous sulphate used as depolarizer were responsible for observed variations in the E.M.F. of Clark cells and this was later emphasized by Swinburn,[1] while Jaeger and Lindeck[2] came to the same conclusions about the cause of the variations in the E.M.F. of cadmium cells, but there was no suggestion as to the nature of the suspected impurity. Some idea as to the nature of the impurity was first had when precautions were taken to avoid the formation of basic mercurous sulphate in preparing the depolarizer and when the specifications for making the cells were altered so as to avoid hydrolyzing the mercurous sulphate in making the paste. Then it was found that the cells had a much greater reproducibility and especially that the high preliminary values and subsequent decrease in E.M.F., characteristic of cells constructed in the old way, had disappeared. These results pointed to the basic salt and hydrolysis as the disturbing elements. The first cells constructed according to these principles were the four (*D*) cadmium cells made in December, 1903, and described, together with the method of construction, in a paper by Carhart and Hulett read at the Washington meeting of the American Electrochemical Society, April, 1904.[3] In February, 1904, twelve (*F*) cells were made and the agreement among themselves and with the (*D*) cells indicated a reproducibility of one part in 100,000; but in time deviations in the values of these cells were observed and in October, 1905, more cells were made according to the same specifications but they had an E.M.F. about one part in

[1] Brit. Association Report, 1901.

[2] Zeit. Instrk., 21, 33.

[3] See also Trans. Amer. Electrochem. Soc., 5, 59. Trans. International Electrical Congress, St. Louis, Vol. 2, 109–126. Zeit. Phys. Chem., 49, 483.

10,000 greater than the older *D* and *F* cells. Some 120 cadmium cells have been made at intervals during the last five years and they have all been kept together in an oil-bath which has very seldom varied .01° from 25°. Some, like the *D* and *F* cells, showed a slow decrease, others have remained constant and again others have shown a marked and steadily decreasing value and have become so low that they have been rejected as entirely worthless. Considering only the cells which have not been rejected a comparison at the present time shows values ranging from 1.01843 to 1.01827 volts, the older ones being the lowest. Cells have been made at the Bureau of Standards [1] and at the National Physical Laboratory [2] according to the principles just indicated. Some of the cells described by F. E. Smith [3] show unmistakably this decreasing E.M.F. and the author was unable to assign a reason for the observed changes, but noticed discolorations in the paste of some of these "abnormal" cells, a phenomenon which has appeared in some of our cells which have fallen to a very low value.

In interpreting the observed decrease in the E.M.F. of these cadmium cells account must be taken of the conditions in the cell. The viscous solution and fine-grained paste so retard diffusion and convection that concentration differences persist and play a decided rôle. It is the layer of solution immediately next to the mercury electrode and its mercury concentration that determines the potential difference in the cathode leg. That this layer in the cadmium cell is different from the rest of the electrolyte in the cathode leg is shown by the rotation experiments. When the system was rotated the solution became of uniform concentration throughout and the E.M.F. observed immediately on stopping the rotation gave the potential difference between mercury and the solution, but as soon as the "paste" settled down on the mercury the potential difference began to decrease, rapidly at first and then more slowly. The clear supernatant liquid however when brought onto a clean mercury electrode still continued to show the original high potential difference against mercury [4] and thus it was seen that only the mercury concentration in the surface layer had changed.

[1] Bull. Bureau of Standards, 4, 1.
[2] Philos. Trans., A, 207, 400.
[3] L. c., 400.
[4] PHYS. REV., 25, 27.

All of these facts may now be readily interpreted by making a a single assumption, namely, that the rate of hydrolysis of mercurous sulphate is accelerated by a plain mercury surface. Basic salt and acid would then form more rapidly in the surface layer than in the rest of the electrolyte and, owing to the difficulty of diffusion from this layer, it would rapidly become saturated and begin to deposit the basic salt and, with the increasing acid concentration in the surface layer, the mercury concentration passed at once into the descending part of curve *I*, Fig. 3.

Thus it is that only decreasing electromotive forces are observed in the cadmium cell. In the rotated system the high values obtained began to decrease as soon as the solids settled down on the mercury and retarded the diffusion of the acid from the surface layer, and this layer came at once into the descending part of the curve. Stirring the paste immediately brought back the high E.M.F. and the true potential between the mercury and the system. When hydrolysis was prevented by the presence of sufficient acid these changes entirely disappeared from the cell and the rotated system and this fact has defeated all attempts to explain the phenomena from the standpoint of oxidation and reduction or as due to surface tension.

The normal solubility of mercurous sulphate in a cadmium sulphate solution was found to be .00214 mole in a liter and no doubt the solution in the paste contains a somewhat greater concentration than this. When saturated with both normal and basic salt the concentration is not far from .004 mole of mercurous mercury in a liter, so it is seen that the surface layer has only a short distance, in quantity, to go to enter the descending part of the curve and the decrease then depends on the amount of the acid generated in the surface layer and the effectiveness of the paste in preventing its diffusion. It is at once seen that diffusion will not cease until the whole system has reached the equilibrium concentration of .08 mole of sulphuric acid in a liter and as this does not take place even under favorable conditions, hydrolysis does not cease and the basic salt continues to form at the expense of the normal salt. This change continues until the normal salt has all disappeared from the vicinity of the electrode and there is the tendency of the surface

layer to approach the very low mercury concentration due to the basic salt, although there is still plenty of normal salt in the paste.

Furthermore there is evidence that the basic salt $Hg_2(OH)_2Hg_2SO_4$ does not remain intact,[1] but suffers further hydrolysis to mercurous oxide and acid. The mercurous oxide is very unstable and in decomposing furnishes the conditions for the formation of the very insoluble basic mercur*ic* sulphate, a bright yellow compound. The yellow coloration, noted by Smith[2] and confirmed by the appearance of some of our cells which have gone to a very low value, we have taken to indicate the presence of this basic mercuric sulphate. The basic mercur*ous* sulphate is colorless or gray.[3] It is quite within the possibilities that these insoluble basic sulphates separate out as incrustations on the mercurous sulphate and cadmium sulphate crystals in the vicinity of the electrode and in this way decidedly effect equilibrium conditions controlled by these salts. It is true that only a certain per cent. of cadmium cells fall to the very low values, although the number increases with the age of the cells. It is not surprising that the phenomenon does not appear in all cells, no more so than the fact that supersaturated solutions, as near alike as we can make them, do not all crystallize. The cause is possibly the same in both cases, as the basic salt need not appear as a solid phase until the solution is supersaturated in respect to it.

| Cell. | Nov. 30. | Dec. 7. | Dec. 12. | Jan. 10. | Feb. 1. | Mar. 1. | Apr. 4. |
|---|---|---|---|---|---|---|---|
| N 1 | 1.01842 | 1.01843 | 1.01841 | 1.01839 | 1.01835 | 1.01822 | 1.01776 |
| N 2 | 44 | 43 | 41 | 45 | 41 | 46 | 830 |
| N 3 | 44 | 41 | 40 | 40 | 35 | 26 | 797 |
| N 4 | 44 | 42 | 40 | 42 | 39 | 34 | 797 |
| N 5 | 43 | 41 | 40 | 44 | 41 | 39 | 808 |
| N 6 | 43 | 42 | 40 | 41 | 41 | 40 | 822 |
| N 7 | 44 | 41 | 40 | 40 | 38 | 37 | 812 |
| N 8 | 43 | 45 | 40 | 36 | 32 | 37 | 828 |
| N 9 | 43 | 40 | 40 | 36 | 31 | 19 | 788 |
| N10 | 43 | 43 | 45 | 45 | 42 | 40 | 823 |

Some cells made in 1904 now become of interest. In order to make cells with a lower internal resistance a coarse-grained paste

[1] Zeit. Phys. Chem., 49, 491.
[2] Trans. Roy. Soc., A, 207, 407.
[3] Zeit. Phys. Chem., 49, 491.

only 3 or 4 mm. deep was used. The mercurous sulphate was formed electrolytically on a large mercury anode in sulphuric acid and with the low current density used these crystals were several days in forming. Ten of these ($N$) cells were made on November 29, 1904, and their record for the first four months follows: These cells were found to be in excellent agreement after two weeks, but soon began to show irregularities and in four months were so irregular and low that observations were discontinued on all but N9 and N10.

| Cell. | 1905 | | | 1906. | | | |
|---|---|---|---|---|---|---|---|
| | June 2 | Nov. 12. | Dec. 14. | May 12. | July 7. | Aug. 14. | Oct. 2. |
| N 9 | 1.01766 | 1.01715 | 1.01722 | 1.01600 | 1.01462 | 1.01364 | 1.01228 |
| N10 | — | 1.01815 | 1.01816 | 1.01813 | 1.01813 | 1.01812 | 1.01810 |

It is interesting to notice that the first comparison of these cells soon after they were made showed values, if anything, slightly higher than the "normal" value of the cadmium cell, so it is to be concluded that coarse crystals and a small amount of them in the paste were nevertheless able to saturate the solution in a comparatively short time, but the conditions were very favorable for diffusion to take place and for the changes just outlined to come into play with the results we would now expect. It was the behavior of these cells particularly that suggested that attention was to be given to the depth of the paste in the cadmium cell.[1]

H. V. Steinwehr[2] found, by grinding the mercurous sulphate to a fine powder, that an increased potential was produced against mercury in a cadmium sulphate solution and he at once concluded that all variations of standard cells were due to the size of grains of the depolarizer. V. Steinwehr then prepared a large-grained mercurous sulphate and selected crystals of a uniform size, but the cells were irregular and inconstant and the author attributed their behavior to the little crystals which grew on the larger ones. From the facts now at hand it is to be concluded that surface tension had very little to do with V. Steinwehr's experiments. Not only is the effect of size of particles not to be feared in constructing the cad-

[1] PHYS. REV., 23, 174.

[2] Z. f. Instrmentenk., 25, 205, and Z. Elektrochem., 1906, 578.

mium cell, but it may be concluded that a rather fine-grained paste of good depth would give the most constant results in the cadmium cell. The old way of washing the mercurous sulphate with water made for constancy in this system as the wash water, which was acid, was not entirely removed in making the paste. That such cells do remain constant is shown by the results just published by Professor Carhart[1] on his (*B*) cells which were made in 1903 and have been constant for over four years. Reproducibility could be obtained by preparing the mercurous sulphate in a definite way and with a fine-grained preparation made to a paste in the old way the cadmium cells would not show the changes now encountered. It is questionable whether the new method of construction gives a sufficiently greater reproducibility to the cadmium cell to justify the attempt to exclude the basic salt from the depolarizer. If the basic salt is formed in the cell after it is constructed there is no point to many of the precautions now taken.

Starting with mercury, mercurous sulphate and a cadmium sulphate solution there is little hope of bringing the system to equilibrium as was shown by the rotation experiments and subsequent analyses. The equilibrium might be approached from the other side if we could start with the components of this system: Hg, $Hg_2O$, $CdSO_4 \frac{8}{3} H_2O$, $SO_3$ and $H_2O$ — but the instability of the mercurous oxide excludes this possibility. A knowledge of the equilibrium conditions of this system has suggested still one further possibility: we may start with a sufficiently acid solution of cadmium sulphate to entirely prevent hydrolysis of the mercurous sulphate and then the system rapidly comes to equilibrium — it is then a nonvariant system when the temperature is fixed and does not show the changes of the cadmium cell. Some 30 of these "acid" cells have been made during the last three years but the latest results show that the acid concentration was too small but none of them have shown a tendency to decrease. One cell was made in October, 1905, with .2 molar sulphuric acid and has shown a constant value of 1.01792 volts. It has not varied over .00003 volt at any time during the three years; at present its value is 1.01793. The only defect so far noticed in these cells is a tendency of the amalgam to

[1] PHYS. REV., 26, 124.

slowly generate hydrogen, about as much as the zinc amalgam does in the Clark cell. There appears to be no way of keeping the acid concentration automatically fixed but this may not be necessary as the cells show no definite evidence of increasing E.M.F. which would result from decreasing acid concentration. In these acid cells a decrease of .004 mole in a liter of the acid concentration would be needed to increase the E.M.F. .00001 volt. These acid cells deserve further investigation for it is evident that the action of the amalgam on the acid solution s a very slow one and the device of using an acid solution for the unsaturated secondary standards has given most satisfactory results.[1]

The results obtained from the experiments (10, 11, 12 and 13) with the cathode system of the Clark cell are plotted in Fig. 3, curve *II*, and it is seen that there is an entirely different state of affairs in this cell. The mercury concentration in the Clark system to which no acid was added represents a solubility only slightly greater than that indicated by the exterpolated curve from the results with the Clark systems with acid. The results embodied in curves *I* and *II*, Fig. 3, independently confirm the rotation experiments and justify the conclusions that were drawn from those experiments; namely, that a cadmium sulphate solution hydrolyzes mercurous sulphate while a zinc sulphate solution does not. Now hydrolysis is of very common occurrence and need not necessarily affect either the reproducibility or constancy of a cell but in the case of the cadmium cell the hydrolysis establishes a state of unstable equilibrium and so sooner or later, depending upon circumstances, changes appear and it is to be concluded that we are dealing with a non-reversible electrode, a point that has now been pretty thoroughly tested.

*Reversibility of the Cathode Systems.* — In 1905 an attempt was made to make mercurous sulphate electolytically in a saturated cadmium sulphate solution instead of in sulphuric acid. It was expected that this method would obviate many of the troublesome operations of making the paste and produce a product which would necessarily be in equilibrium with a cadmium sulphate solution. But the cells made up with these preparations as depolarizers had a

[1] PHYS. REV., 27, 33.

high value and did not remain constant but decreased as may be seen from the published results[1] and it may be added that they have since decreased. These results were most puzzling at the time, they showed that with rapid stirring and a low current density the mercurous sulphate formed at a mercury anode in a saturated cadmium sulphate solution was not in equilibrium with the solution and the reaction was not a reversible one while all the experiments with the Clark cell indicate that its cathode system was reversible. An attempt has been made to directly compare the two cells from the standpoint of reversibility. Both Clark and cadmium cells were made without depolarizers, that is, the mercury cathode was covered with coarsely crushed zinc sulphate crystals and the saturated solution, while the anode was of the usual construction. The cadmium cells were made in the same way and were of the same pattern and dimensions. These cells were fastened to a motor-driven shaker so regulated that the mercury of the cathode and the materials above it were in constant and uniform motion, then these cells were all charged with the same current, .020 amp. to a cm.$^2$ mercury surface. The mercurous sulphate formed soon saturated the solution and then separated as a solid and was mixed with the crystals of zinc or cadmium sulphate. The motion and low current density offered favorable conditions for forming the normal sulphate, after about .100 mg. had formed in each cell, the charging current was broken and the cells placed in the 25° bath. The paste formed in this way was white in color and about 4 mm. deep. Two cadmium cells were made together in series, WN1 and WA; the first was neutral while WA had been made up with .1 molar sulphuric acid. Later WN2, a neutral cadmium cell, was made in the same way, and the two Clark cells, S1 and SH were made up without acid and then the depolarizer formed in the cell as indicated.

The two cadmium cells with neutral solutions, WN1 and WN2, were very high at first and steadily decreased and are still decreasing. There was no suggestion of stopping at the "normal" value of the cadmium cell which is 1.01840 at 25° and this emphasizes the conclusions to be drawn from the rotation experiments, that this value 1.01840 is the value the cells have when put up in a particu-

[1] PHYS. REV., 23, 175.

lar way and is not an equilibrium value. (After the observations of June 6 the pastes in these cells were stirred by shaking the cell and WN2 particularly at once increased but only to subsequently decrease.) The behavior of WA, the cell made with .1 molar sulphuric acid, is quite different; it had a high preliminary value indicating that some basic salt was formed and the E.M.F. decreased but came to a constant value at about 1.01830, which is about the equilibrium value for cells with this amount of acid. The Clark cells, S1 and SH, have been quite constant and the differences between the Clark and cadmium cells is as marked here as in the rotation experiments. These results with the acid cadmium cell and Clark cells suggest that it may be possible to construct these cells and form the depolarizer electrolytically in the cell after they are set up and this would entirely avoid the troublesome manipulations and uncertainties incident to preparing the mercurous sulphate and paste.

| Cell. | Date. | Jan. 6. | Jan. 9. | Jan. 20. | Feb. 6. | Feb. 18. | Mar. 5. | Mar. 2. |
|---|---|---|---|---|---|---|---|---|
| WN1 | Jan. 5 | 1.01992 | 1.01974 | 1.01926 | 1.01861 | 1.01827 | 1.01755 | 1.01675 |
| WN2 | Mar. 12 | | | | | | | 1.01890 |
| WA | Jan. 5 | 1.01903 | 1.01883 | 1.01873 | 1.01826 | 1.01828 | 1.01828 | |
| S1 | | | | | 1.42082 | 1.42084 | 1.02086 | 1.42080 |
| SH | | | | | 80 | 88 | 89 | 88 |

| Cell. | Date. | Apr. 8. | May 3. | June 6. | June 30. | July 14. | Aug. 18. |
|---|---|---|---|---|---|---|---|
| WN1 | Jan. 5 | 1.01190 | 1.9705 | 1.9644 | .9531 | .9255 | |
| WN2 | Mar. 12 | 1.01863 | 1.01848 | 1.01770 | 1.01813 | 1.01757 | 1.01611 |
| WA | Jan. 5 | 1.01821 | 1.01829 | 1.01831 | 1.01851 | 1.01854 | 1.01859 |
| S1 | | 1.42080 | 1.42077 | 1.42071 | 1.42080 | 1.42072 | 1.42068 |
| SH | | 87 | 86 | 79 | 79 | 71 | 70 |

*The Clark Cell.* — The Clark cell has been subjected to most searching tests in the investigations on standard cells and it is to be noted that the rotated cathode system showed variations of from .00005 to .00010 volt and that the E.M.F. of the rotated system was always slightly greater than that of the adjustable cell which contained the same materials. The analysis of the liquid of the rotated system showed .837 g. mercurous sulphate in a liter of the solution while the curve *II*, Fig. 3, gives as the solubility of normal

mercurous sulphate in the cathode system of the Clark cell at 25°, .00166 mole or .8234 g. in a liter, a measurably lower value. Also the cells just described, S1 and SH, where the mercurous sulphate was made electrolytically in the cell, are not quite normal as the E.M.F. is noticeably higher than the normal value for 25° which is for the Clark cell 1.42040 volts. These deviations are all in the same direction and suggest that a zinc sulphate solution does not entirely prevent a mercurous sulphate from hydrolyzing, but this is probably so slight that equilibrium conditions are established before there is a separation of the basic salt, for the severe tests to which this cell has been subjected lead to the conclusion that this cathode system does come to equilibrium and is essentially reversible. The components of this system may then be taken as mercury, mercurous sulphate, zinc sulphate and water — and at a given temperature it is non-variant. But we cannot take the corresponding substances as components for the cadmium cell cathode system, for, when the hydrolysis is sufficient to produce the basic salt as a solid phase and the acid remains in solution, it diffuses to the anode; then these substances are no longer in stoichiometrical relations in the system, and so the products of hydrolysis must be taken as components and the final product due to the interaction with water in the mercurous oxide, which is unstable and the reaction is not reversible. So there seems little hope of obtaining equilibrium with this system unless acid is added to it, and there probably would not be the possibility of equilibrium in the Clark cell if the basic salt appeared as a solid.

The first Clark cells which were constructed with attention to excluding the basic salt from the depolarizer were the twelve (*H*) cells made on March 15, 1904, and at intervals since then cells have been made according to the same principles. At the present time these cells show no deviations greater than one part in 50,000 and this is the best of evidence that these Clark cells furnish a constant and reproducible basis of electromotive force. Their value has been assumed to be 1.42040 volts at 25° and they have been the standard of reference for all previous E.M.F. measurements. The temperature coefficient of the Clark cell is about a millivolt per degree and this was a real objection to the cell before the introduction of thermostats and was the chief reason for the popularity of

the cadmium cell with its much lower temperature coefficient, but for the exact measurements of the present day a thermostat is necessary for any but the Weston secondary cell. The thermostat used for this work is reliable to .01° and such variations indicate an uncertainty of less than one part in 100,000 of the E.M.F. of the Clark cell. The tendency of the glass to crack, where the amalgam contact wire is sealed in, has appeared in the older cells and made it necessary to reject many of them; this and other points in the construction of Clark cells may best be considered in a separate article.

PRINCETON UNIVERSITY,
August, 1908.

# STUDIES IN LUMINESCENCE.

By Edward L. Nichols and Ernest Merritt.

## X. The Phenomena of Phosphorescence Considered from the Standpoint of the Dissociation Theory.[1]

By Ernest Merritt.

In an important paper on luminescence published in 1895 Wiedemann and Schmidt[2] have suggested that in many instances, notably in the case of solid solutions, the effect of light, or of other exciting agents, is to produce electrolytic dissociation of the dissolved active substance, and that the light emitted during luminescence is to be explained as the result of the molecular vibrations which occur either during the process of dissociation or when the ions recombine. Wiedemann and Schmidt discussed the various types of luminescence in considerable detail and showed that the theory proposed by them will account for the phenomena, at least qualitatively, in a very satisfactory way.

In one of the previous papers of this series it was pointed out that this theory leads to a simple explanation of Stokes' Law,[3] which has usually proved a stumbling block in the development of theories of luminescence; and some progress was also made toward the development of a quantitative theory of phosphorescence on the basis of the dissociation hypothesis.

In view of what has already been accomplished by the theory of Wiedemann and Schmidt it appears to the writer that this theory is by far the most promising of those that have yet been proposed. In discussing the theoretical significance of the observations on phosphoresence described in the preceding papers of this series, it has therefore seemed advisable to use this theory as a basis.

The present paper is devoted chiefly to a discussion of the theory of phosphorescence. No attempt will be made to develop a complete theory. It is intended rather to consider in turn the various

[1] The ninth paper of this series, whose publication has been unavoidably delayed, will appear in the near future.

[2] Ann. der Phys., Vol. 56, p. 177, 1895.

[3] Nichols and Merritt, Phys. Rev., Vol. 22, p. 279, 1906.

factors which may have an influence on the phenomena, and to determine so far as possible the nature of this influence. Comparison with experimental results will then make it possible to form an opinion of the relative importance of the various factors considered.

It will facilitate the discussion if we consider first the requirements which a satisfactory theory must meet. The most important experimental results in the case of photoluminescence are briefly mentioned below.

### SUMMARY OF EXPERIMENTAL LAWS.

1. Stokes' Law.

2. If we isolate a single band of the luminescence spectrum it is found that the distribution of intensity throughout the band is independent of the intensity and wave-length of the exciting light.[1]

3. The light emitted during the luminescence of an isotropic substance is unpolarized, whatever may be the condition of polarization of the exciting light.

4. During the decay of phosphorescence each band of the luminescence spectrum behaves as a unit; *i. e.*, the wave-length of maximum intensity and the relative distribution of intensity throughout the band remain unchanged.[2]

The theoretical aspect of these general laws was discussed in the sixth paper of this series,[3] and it was then pointed out that the laws are directly deducible from the dissociation theory.

To these four general laws must be added the following experimental facts connected with the decay of phosphoresence :[4]

5. *Form of Decay Curve.* — The curve obtained by plotting the values of $I^{-\frac{1}{2}}$ as ordinates and the corresponding values of $t$ as abscissas is a straight line for small values of $t$; it changes to a curve concave towards the axis of $t$ as $t$ increases; but for still larger values of $t$ the relation between $I^{-\frac{1}{2}}$ and $t$ is again linear, and remains so until $I$ becomes too small to measure. In other words the decay curve is dependent on the intensity and duration of ex-

[1] This law, first enunciated by Lommel, is discussed in the second and third articles of this series. See PHYS. REV., Vol. 18, p. 403, and Vol. 19, p. 18.

[2] Nichols and Merritt, PHYS. REV., Vol. 21, p. 247.

[3] PHYS. REV., Vol 22, p. 279.

[4] Nichols and Merritt, PHYS. REV., Vol. 22, p. 279; Vol. 23, p. 37; Vol. 25, p. 362.

citation. The slant is altered in each of the straight parts by a change in either of these two factors in the excitation.

6. *Hysteresis.* — The behavior of a phosphorescent substance with a given excitation depends upon its previous history. Some semi-permanent change is produced by excitation which persists for several hours, or even for several days, after visible phosphorescence has ceased.

7. *Effect of Red and Infra-red Rays.* — In the case of certain substances the semi-permanent condition produced by excitation may be destroyed and the material restored to a standard state by a brief exposure to the red and infra-red rays. The effect of the longer waves [1] during phosphorescence is to accelerate the decay. In some substances, but not in Sidot blende, the first effect is to increase the brightness of phosphorescence, this temporary effect being followed by decay more rapid than the normal.

## Becquerel's Explanation of the Form of the Decay Curve.

In the case of a homogeneous substance free from any disturbances due to absorption and diffusion it is readily shown that the decay of phosphorescence, as predicted by the dissociation theory, should follow the law [2]

$$I = \frac{1}{(a + bt)^2}$$

where $I$ is the intensity of phosphorescence at any time $t$ after the end of excitation. This law, first proposed as an empirical relation by E. Becquerel, has also been derived by H. Becquerel on the basis of an entirely different theory.[3]

The decay of phosphorescence in gases appears to be strictly in accordance with this law.[4] Under certain special conditions as regards temperature, etc., the law is very closely obeyed by zinc sulphide [5] and even by Balmain's paint.[6] But in the great majority of

[1] Although the rays that produce these effects are generally of longer wave-length than the rays that excite luminescence, this is not always the case. Several exceptions are cited by Dahms.

[2] Nichols and Merritt, Phys. Rev., Vol. 22, p. 279, 1906.

[3] H. Becquerel, Compt. Rend., Vol. 113, p. 618, 1891.

[4] C. C. Trowbridge, Phys. Rev., Vol. 26, p. 515, 1908.

[5] C. A. Pierce, Phys. Rev., Vol. 26, p. 312, 1908.

[6] C. A. Pierce, Phys. Rev., Vol. 26, p. 454, 1908.

instances the phosphorescence of solids decays in accordance with a more complicated law. As stated above the curve obtained by plotting values of $I^{-\frac{1}{2}}$ as ordinates and the corresponding values of $t$ as abscissas is not linear throughout, as the simple theory would lead us to expect. The curve is straight both for small values of $t$ and for large values of $t$, but shows a sharp curvature for intermediate values.

It has been suggested by H. Becquerel that this form of curve is to be accounted for by assuming that the phosphorescence spectrum consists of two bands, each of which obeys the simple law, but having different rates of decay. If a decay curve is plotted for each of the two assumed bands the equations of the two curves will be

$$I_1^{-\frac{1}{2}} = a_1 + b_1 t \quad \text{and} \quad I_2^{-\frac{1}{2}} = a_2 + b_2 t$$

and each of the two curves will be a straight line. But if we plot $I^{-\frac{1}{2}}$ against $t$, where $I$ is the observed *total* intensity ($I = I_1 + I_2$)

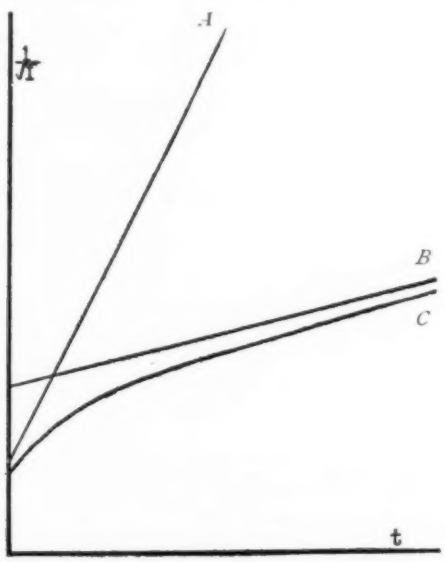


Fig. 69. Illustrating Becquerel's explanation of the form of the decay curve in solids.

the resulting curve will not be straight but will take the form shown by curve $C$, Fig. 69. In this figure curves $A$ and $B$ are the decay curves for the two bands taken separately. In the case

represented in the figure the two bands are assumed to decay at widely different rates, and the band which decays more rapidly ($A$) has initially the greater intensity. It will be seen that under these circumstances the decay curve for total intensity has all the characteristics of the curves determined by experiment. Becquerel cites one substance for which the observed intensity can be represented by the expression

$$I = \frac{1}{(a_1 + b_1 t)^2} + \frac{1}{(a_2 + b_2 t)^2}$$

with remarkable accuracy. In the case of this particular substance Becquerel also found independent evidence of the existence of two bands in the phosphorescence spectrum.

This way of accounting for the form of the decay curve was also proposed by Pierce in discussing the decay of phosphorescence in Emanationspulver, and has been shown by him to give a very satisfactory explanation of the change in the form of the decay curve resulting from changes in temperature.

In the case of our own observations on Sidot blende we have expressed the opinion that the curves obtained are to be regarded as showing the decay of the green band alone; for although Sidot blende also possesses bands in the blue and violet, these decay so quickly and are of such small luminosity that they can scarcely affect the curves to any appreciable extent. In the more recent work of Werner[1] special precautions were taken in the choice of a substance and in the use of color screens to make certain that one band only was studied; yet the curves obtained are of exactly the same type as those found by other observers.

The work of Werner, even more strongly perhaps than our own work with Sidot blende, thus appears to discredit any explanation of the form of the decay curve that is based upon the assumption of two bands in the phosphorescence spectrum. It cannot be denied, however, that two bands may well be present even when special precautions of this kind are taken, and even when the spectrophotometer shows no indication of a double band. The bands of a phosphorescence spectrum are ordinarily so broad that two bands lying close together might readily appear as one. If the

[1] A. Werner, Ann. der Phys., Vol. 24, p. 164, 1907.

case is one where the bands actually overlap it would be impossible to make observations on one alone without working at the extreme edge of the double band, where the intensity would probably be too small to permit of accurate observations. I am at present unable to see any method of directly testing the matter. Since the assumption of two nearly coincident bands offers so direct an explanation of the form of the decay curve, and since it seems certain that curves may be plotted on the basis of this assumption which deviate from the observed curves by less than the experimental errors, it must be admitted that the hypothesis has much in its favor.

There are several reasons, however, for looking upon this explanation of the form of the curve with suspicion. In the first place it does not account either for the remarkable changes produced in the decay curves by varying the intensity and duration of excitation, or for the phenomena of hysteresis that have been observed in almost all cases of long time phosphorescence. It also leaves untouched the question of the effects produced by exposure to the longer waves. An even more serious objection is the fact that it is necessary to assume the existence of two nearly coincident bands in *all* cases of long time phosphorescence; for upon replotting the decay curves obtained by different observers with $I^{-\frac{1}{2}}$ and $t$ as coördinates it is found that the curves are of the same type for all substances that have thus far been tested. It is hardly credible that this is accidental. Only two explanations appear to me to be possible: either the existence of two nearly coincident bands is an essential characteristic of substances showing long time phosphorescence, or else the peculiarities exhibited in the form of the decay curve are to be explained in some manner which does not involve the assumption of two bands at all. While it may prove of interest at some later time to develop the theory along the lines suggested by the first of these alternatives, the present discussion will be based upon the acceptance of the second, and I shall consider in what ways the form of the decay curve, as well as certain other peculiarities of phosphorescence, may be explained in substances possessing only one band in the phosphorescence spectrum.

## Absorption Effects.

If a homogeneous substance possessing only one band in its phosphorescence spectrum is uniformly excited throughout, and if the light emitted by the interior portions suffers no diminution by absorption before reaching the surface, then according to the dissociation theory here considered the decay of phosphorescence will be in accordance with the law

$$\frac{1}{\sqrt{I}} = a + bt.$$

These conditions, however, can never be exactly attained. The exciting light must be absorbed to some extent, for otherwise no energy would be available to produce phosphorescence. The excitation will therefore be greatest at the surface, and will diminish, at a rate determined by the absorbing power of the material, as we pass to points within. Since the ions are in consequence more numerous in the surface layers, and since the number of recombinations per second, which determines the intensity of phosphorescence, is proportional to the square of the number of ions, it is clear that the light emitted during the early stages of decay will come chiefly from the surface. As decay proceeds, however, the relatively high rate of recombination at points where $n$ is large will cause a rapid approach to uniformity of ionic concentration, and the part contributed to the total light by the interior of the mass will become increasingly important. At first the intensity of phosphorescence is approximately proportional to $V_1 a n^2$, where $V_1$ is the volume of the surface layer that is chiefly effective. Later, when the light from the interior becomes comparable in intensity with that from the surface, the phosphorescence will be approximately proportional to $V_2 a n^2$, where $V_2 > V_1$. In terms of the total number of ions, $N$, the two intensities will thus be approximately proportional to $a/V_1 \cdot N^2$ and $a/V_2 \cdot N^2$. So far as the slant of the decay curve is concerned this is equivalent to a decrease in the coefficient of recombination and will result in making the curve concave toward the axis of $t$. Absorption of the emitted light will complicate the phenomena but will not modify the general result. The effect of absorption is therefore to produce a change in the

form of the decay curve which is at least in the right direction to account for the observed deviation from linearity.

In discussing the effect of absorption in detail I shall assume that both the exciting light and the emitted light suffer absorption, the two coefficients of absorption being $\beta$ and $\gamma$ respectively. At any depth $x$ below the surface the intensity of the exciting light will be

$$E = E_0 e^{-\beta x}.$$

Assuming that ions are produced at a rate proportional to $E$ and that excitation has proceeded for a sufficient time to produce a steady condition, the number of ions per cubic centimeter at any depth $x$ will be determined by the equation

$$\frac{dn}{dt} = 0 = hE - an_0^2 = hE_0 e^{-\beta x} - an_0^2,$$

$$n_0 = \sqrt{\frac{hE_0}{a}}\, e^{-\frac{1}{2}\beta x}.$$

If $n$ is the number of ions per cubic centimeter at the time $t$ we have

$$n = \frac{1}{1/n_0 + \alpha t},$$

and the light emitted per unit volume, denoted by $i$, is

$$i = pan^2 = \frac{p\alpha}{(1/n_0 + \alpha t)^2},$$

$p$ being the light emitted as the result of one recombination.

Since the emitted light suffers absorption the amount contributed to the total observed intensity by a layer of thickness $dx$ will be

$$idxe^{-\gamma x} = \frac{p\alpha e^{-\gamma x} dx}{(1/n_0 + \alpha t)^2}$$

and the total intensity is

$$I = p\alpha \int_0^\infty \frac{e^{-\gamma x} dx}{(ae^{\frac{1}{2}\beta x} + at)^2} = p\alpha \int_0^\infty \frac{e^{-\gamma x} e^{-\beta x} dx}{(a + ate^{-\frac{1}{2}\beta x})^2},$$

where

$$a = \sqrt{\frac{a}{hE_0}}.$$

Putting

$$ate^{-\beta x/2} = z$$

so that

$$dz = -\frac{a\beta t}{2} e^{-\frac{\beta x}{2}} dx \quad \text{and} \quad e^{-\gamma x} = \left(\frac{z}{at}\right)^{\frac{2\gamma}{\beta}},$$

$$I = -\frac{2pa}{\beta(at)^{m+2}} \int_{at}^{0} \frac{z^{m+1} dz}{(a+z)^2},$$

where $m = 2\gamma/\beta$.

Successive partial integration gives

$$I = -\frac{2pa}{\beta(at)^{m+2}} \left[ \frac{1}{m+2} \frac{z^{m+2}}{(a+z)^2} + \frac{2}{m+2 \cdot m+3} \frac{z^{m+3}}{(a+z)^3} + \frac{2 \cdot 3}{m+2 \cdot m+3 \cdot m+4} \frac{z^{m+4}}{(a+z)^4} + \cdots \right]_{at}^{0}.$$

Upon putting in the limits this becomes

$$I = \frac{2pa}{(m+2)\beta} \cdot \frac{1}{(a+at)^2} \left[ 1 + \frac{2}{m+3} \cdot \frac{at}{a+at} + \frac{2 \cdot 3}{m+3 \cdot m+4} \left(\frac{at}{a+at}\right)^2 + \cdots \right].$$

The series in the brackets has the value 1 for $t = 0$ and as $t$ becomes large approaches the series

$$1 + \frac{2}{m+3} + \frac{2 \cdot 3}{m+3\, m+4} + \cdots = S.$$

If the decay curve is plotted in the usual way with $I^{-\frac{1}{2}}$ and $t$ as coördinates it is clear that the change in slant in passing from small values of $t$ to large values will depend upon $S$ and will be greatest when $S$ is greatest. The maximum deviation from linearity in the form of the decay curve which can result from absorption will therefore be produced when $m = 0$, *i. e.*, when $\gamma = 0$. To determine whether absorption is sufficient to account for the observed type of curve I shall therefore consider first this special case for which the effect is greatest.

For $m = 0$ we have

$$I = -\frac{2pa}{\beta(at)^2} \int_{at}^{0} \frac{z dz}{(a+z)^2} = -\frac{2pa}{\beta(at)^2} \left[ -\frac{z}{a+z} + \log(a+z) \right]_{at}^{0}.$$

Putting in the limits this becomes

$$I = \frac{2p\alpha}{\beta(at)^2}\left[\log\left(1+\frac{at}{a}\right) - \frac{\frac{at}{a}}{1+\frac{at}{a}}\right].$$

Writing $\theta$ for $at/a$

$$I = \frac{2p\alpha}{a^2\beta}\cdot\frac{1}{\theta^2}\left[\log(1+\theta) - \frac{\theta}{1+\theta}\right].$$

The curve for $\theta$ and $I^{-\frac{1}{2}}$, computed in accordance with this equation, is plotted in Fig. 70, the quantity $2p\alpha/a^2\beta$ being put equal to unity. This curve may be looked upon as showing the relation between $I^{-\frac{1}{2}}$ and $t$ for $\alpha/a = 1$. The curve for any different value

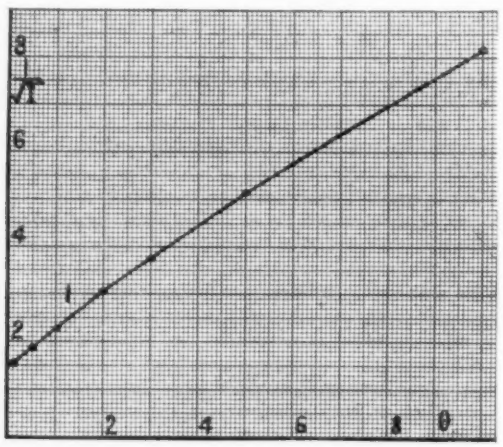


Fig. 70. Showing the greatest deviation from linearity in the decay curve which can be produced by absorption alone.

of $\alpha/a$ may then be found by changing the vertical and horizontal scales to correspond to the change in $\alpha/a$.

The curve of Fig. 70 is similar in form to the decay curves observed in the case of short excitation. Pierce[1] has also observed curves of nearly this form with zinc sulphide. It is possible, there-

[1] C. A. Pierce, PHYS. REV., Vol. 26, p. 314, Fig. 1. In our own work with this same substance, "Emanationspulver," we found a decay curve of the usual type, *i. e.*, with a well marked "shculder" at $t = 20$ sec. (PHYS. REV., Vol. 28, p. 50, Fig. 51). It is interesting to inquire whether the difference is due to the repeated heating and cooling to which Pierce's material was subjected.

fore, that the relatively slight deviation from linearity in such cases is to be ascribed to absorption. But in the case of the majority of decay curves it is clear that absorption is not to be regarded as an important factor; for no change of scale can bring about any close resemblance between the curve of Fig. 70 and the decay curves usually observed for long and moderately long excitation.

### Influence of Irregularities in the Distribution of the Active Material.

Luminescent substances are in most cases solid solutions. In fact it is doubtful whether luminescence can occur in an absolutely pure substance. Pure calcium sulphide for example is not phosphorescent; but the addition of a small amount of some other metal, such as manganese or copper, gives it the power to phosphoresce brilliantly. The method of preparating the phosphorescent sulphides is such as to bring about a very intimate mixture of the constituents, and it is natural to think of the manganese, copper, or other active material as being dissolved in the sulphide.

So little is known regarding the nature of solid solutions that we cannot say with certainty whether such substances are to be regarded as strictly homogeneous or not. Especially in the case of crystals it seems not improbable that the molecules of the solute may not be uniformly distributed throughout the mass of the solvent, but may to a greater or less extent collect in groups or minute crystals. Any lack of uniformity in the distribution of the active substance will cause a corresponding variation in the concentration of the ions produced by the exciting light; and if the nature of the solvent is such as to permit of diffusion the phenomena will be complicated by the fact that a redistribution of the ions will occur during excitation and decay. Even without diffusion, however, the form of the decay curve will be modified. For since the rate of recombination is proportional to the square of the ionic concentration the intensity of phosphorescence will decay at different rates in different parts of the mass. The effect on the decay curve will be similar to that produced by absorption; in fact the decay curve is modified by absorption of the exciting light only because of the resulting lack of uniformity in the ionic concentration at different depths below the surface.

Our complete ignorance of the distribution of the active material makes it almost useless to attempt any exact treatment of the problem. It is possible, however, without questionable assumptions or great analytical complexity to predict the general character of the effect to be expected.

Let $n$ be the number of ions per unit mass at any point; $n$ is then some unknown function of the position of the point in question and of the time that has elapsed since the decay began. The number of recombinations per second will be $\alpha n^2$ per unit volume, and the number of recombinations for the whole mass will be $\int \alpha n^2 d\tau$, where $d\tau$ is an element of volume. Disregarding the absorption of the emitted light we have

$$I = k\alpha \int n^2 d\tau.$$

Since ions are destroyed only by recombination

$$\frac{dN}{dt} = -\alpha \int n^2 d\tau$$

where $N$ is the total number of ions.

If $\bar{n}$ is the volume average of $n$, and $\bar{n^2}$ the volume average of $n^2$, so that

$$\bar{n} = \frac{1}{\tau}\int n d\tau = \frac{N}{\tau}, \quad \bar{n^2} = \frac{1}{\tau}\int n^2 d\tau, \quad \frac{dN}{dt} = -\alpha\tau\bar{n^2}.$$

If we put

$$\rho = \frac{\bar{n^2}}{(\bar{n})^2}, \quad \bar{n^2} = \rho(\bar{n})^2 = \rho\frac{N^2}{\tau^2} \quad \text{and} \quad \frac{dN}{dt} = -\alpha\tau\rho\frac{N^2}{\tau^2} = -\frac{\alpha\rho}{\tau}N^2,$$

$$\frac{1}{N} - \frac{1}{N_0} = \frac{\alpha}{\tau}\int_0^t \rho dt.$$

Writing $\rho_1$ for the average value of $\rho$ between $o$ and $t$

$$N = \frac{1}{\frac{1}{N_0} + \frac{\alpha\rho_1}{\tau}t}, \quad I = -k\frac{dN}{dt} = \frac{k\alpha}{\tau}\cdot\frac{\frac{d}{dt}(\rho_1 t)}{\left(\frac{1}{N_0} + \frac{\alpha\rho_1}{\tau}t\right)^2}.$$

Since

$$\rho_1 = \frac{1}{t}\int_0^t \rho dt, \qquad \frac{d}{dt}(\rho_1 t) = \rho$$

$$\therefore \frac{1}{\sqrt{I}} = \sqrt{\frac{\tau}{k\alpha\rho}}\left(\frac{1}{N_0} + \frac{\alpha\rho_1}{\tau}t\right).$$

Although we are unable to determine $\rho$ and $\rho_1$ as functions of $t$ it is clear that both will decrease as $t$ increases. It is clear also that the change will become less rapid as the decay proceeds, and that both $\rho$ and $\rho_1$ will sooner or latter become nearly constant. When $I^{-\frac{1}{2}}$ is plotted against $t$ we shall therefore obtain a curve which is concave downward and which finally becomes a straight line. In other words the decay curve will agree in form with the curves determined by experiment.

The effect upon the decay curve of an irregular distribution of the active substance may be illustrated by the following simple case. Let the active material be uniformly distributed except that small regions occasionally occur where the concentration is abnormally large. The whole volume may thus be divided into two parts, $v_1$ and $v_2$. The distribution of the active material is uniform throughout each part, but the concentration in $v_1$ is different from that in $v_2$. When the substance is excited to phosphorescence the ionic concentration will also differ in the two regions. Let the number of ions per cubic centimeter at the end of excitation be $n_1$ in the volume $v_1$ and $n_2$ in the volume $v_2$. Throughout the region $v_1$ the intensity of the light emitted per cubic centimeter will be

$$i = \frac{ak}{(1/n_1 + at)^2}$$

and the *total* intensity at any instant due to this part of the whole mass will be

$$I_1 = \frac{akv_1}{(1/n_1 + at)^2}.$$

The light emitted by the volume $v_2$ is given by the similar expression

$$I_2 = \frac{akv_2}{(1/n_2 + at)^2}$$

and the total intensity is

$$I = I_1 + I_2 = ak\left(\frac{1}{(a_1 + b_1 t)^2} + \frac{1}{(a_2 + b_2 t)^2}\right)$$

where

$$a_1 = \frac{1}{n_1\sqrt{v_1}}, \qquad a_2 = \frac{1}{n_2\sqrt{v_2}},$$

$$b_1 = \frac{\alpha}{\sqrt{v_1}}, \qquad b_2 = \frac{\alpha}{\sqrt{v_2}}.$$

It thus appears that the form of the decay curve is the same as though the substance possessed two bands, coincident as regards wave-length, but differing in rate of decay.

It is not at all unlikely that a condition approaching that assumed in this illustrative case actually exists in most phosphorescent substances. Upon considering the method used in preparing the phosphorescent sulphides, for example, it seems probable that the distribution of the active substance will be far from uniform. When the mixture is first prepared, and before calcination, the active material is unquestionably in the form of small discrete masses distributed irregularly through the mixture. Upon heating to redness diffusion will occur to a greater or less extent, depending upon the temperature and the duration of heating. But even at high temperatures this will be a slow process, and considerable variations in concentration are likely to remain even after prolonged heating. It is to be expected, therefore, that the phosphorescent sulphides will contain numerous nuclei of high concentration surrounded in each case by a region where the concentration is relatively small.[1]

After calcination it is often noticed also that the phosphorescence is very far from being uniform throughout the mass. Owing probably to accidental differences in concentration, or to differences in the heat treatment, the phosphorescence often differs greatly in intensity and even in color in different parts of the same mass. A phosphorescent powder made from such a mass, while presenting the appearance of homogeneity to the unaided eye, would differ

[1] Since a more complete diffusion of the active material will result from prolonged heating it is to be expected, other conditions being the same, that the duration of phosphorescence will be prolonged by increasing the time of heating. This agrees with the facts observed in the preparation of the phosphorescent sulphides.

greatly from point to point in the concentration of the active material.[1] Even if the mixture were so perfect that the microscope could detect no irregularities a wide deviation from linearity in the decay curve is to be expected. It is a significant fact that with one exception all decay curves thus far recorded have been determined with powders prepared in practically the same way that the phosphorescent sulphides are prepared. In fact most of the substances tested were sulphides. The exception noted above was natural willemite[2] in which case the variation in brightness over the surface tested was plainly visible.

It thus appears that irregularities in the distirbution of the active substance are sufficient to explain the deviation from linearity in all the decay curves thus far observed. Such irregularities of distribution are not merely probable, but in many cases are perfectly obvious. But while the distribution of the active material is probably in all cases an important factor, it cannot be the only factor of importance. With Balmain's paint, Pierce has found that the decay curve, which possesses the usual shoulder at ordinary temperatures, becomes almost exactly linear at a temperature of 74°,[3] while for higher temperatures it again shows a curvature of the usual kind. It appears highly improbable that such changes are brought about by temporary changes in the distribution of the active substance. Non-uniformity in the distribution of the active material also offers no explanation of the phenomena of hysteresis or of the effect of the infra-red rays.

[1] While we are chiefly concerned at present with the influence of lack of homogeneity upon the decay curve, it can scarcely be doubted that the effect upon the phosphorescence spectrum is fully as important. For some reason different parts of the mass are differently affected by the process of calcination. This may be due to differences in concentration throughout the mass, or to the fact that the effect of the surrounding gas varies from point to point. When such a mass is powdered and mixed the effect is the same as though we were to make an intimate mixture of several entirely different phosphorescent substances. Each constituent has its own band or group of bands, characterized by definite wavelengths and periods of decay, which differ according to the conditions of preparation. It is not surprising that the phosphorescence spectrum of such a material is complex; and we can scarcely expect simple laws to apply to any of the phenomena exhibited by such a mixture.

[2] The decay of phosphorescence in a speciman of willemite possessing a long time phosphorescence has been studied by Nichols and Merritt, PHYS. REV., Vol. 23, p. 52, Fig. 53. Willemite whose phosphorescence dies out with great rapidity has been studied by Waggoner, PHYS. REV., Vol. 27, p. 209.

[3] PHYS. REV., Vol. 26, p. 458, Fig. 26.

### DIFFUSION EFFECTS

Whenever irregularities exist in the distribution of the active substance there will be a tendency for diffusion to occur. Under ordinary conditions this tendency is probably neutralized by forces which act to keep the distribution unaltered, so that so long as the substance remains in the molecular form the condition is to be regarded as a stable one for the temperature and pressure at which the phosphorescent substance normally exists.

But when the material is excited to luminescence a part of the active substance will be dissociated, and since the resulting ions will possess a different mobility and will be acted upon by different forces from those that determine the behavior of the original neutral molecules, the condition of equilibrium will be destroyed, and some change in the distribution of the active substance is to be expected.

An exact discussion of the effects of diffusion would present great difficulties; for the fact that diffusion and recombination occur at the same time greatly complicates the analytical treatment. It is probable also that in crystals the diffusion constant will be different for different directions. It is clear, however, that the influence of diffusion upon the form of the decay curve must be similar to that produced by an irregular distribution of ions without diffusion. In fact the discussion of the preceding section applies without modification to the case of substances in which diffusion of the ions may occur. Diffusion, however, will increase the rapidity with which uniformity of ionic concentration is approached during decay; and since diffusion will be most active when large concentration gradients exist, the effects of diffusion will be greatest in the early stages of decay. In cases where diffusion is an important factor we should therefore expect a sharper curvature in the early part of the curve, and a more rapid approach to linearity, than in cases where diffusion is absent.

It is not impossible that diffusion is sometimes important even when there is practically complete uniformity in the distribution of the active substance. Owing to the absorption of the exciting light the ionization produced in the surface layer will be more intense than that produced at points beneath the surface. If the absorption is large a large gradient may thus be produced in the ionic con-

centration, and diffusion from the surface layers inward will bring about a change in the decay curve similar in character to that caused by irregularities in the distribution of the active substance. Diffusion produced in this way would ultimately result in an appreciable diminution in the surface concentration of the active material, and we should therefore expect that the intensity of luminescence would be diminished in such a substance by prolonged excitatation. No effect of this kind has been observed by us in the case of Sidot blende, but the observations of Werner[1] with a SrZn compound show evidence of fatigue resulting from prolonged excitation.

The change in the form of the decay curve due to changes in the duration of excitation may be explained, at least in a general way, as a result of diffusion. Diffusion of the ions will occur during excitation as well as during decay. After prolonged excitation, therefore, the volume occupied by ions will be greater than after short excitation, and the rate of decay — in other words the slant of the decay curve — will be correspondingly reduced.[2]

Diffusion also offers an explanation of the phenomena of hysteresis in phosphorescence substances. After prolonged excitation and subsequent decay the neutral molecules that result from recombination will be distributed through a larger volume than before. Since the original distribution of the active material was a stable one there will be a gradual return to the normal distribution. But this will be a slow process and may well require several days for its completion. In the mean time the material is in such a condition that the decay following renewed excitation will be more gradual than the normal, even for a short excitation. The spreading out of the active substance by diffusion, which would normally require a long excitation, has already been accomplished by the preceding excitation, whose effects have not yet disappeared. Hys-

[1] Werner, A., Ann. der Phys., Vol. 24, p. 164, 1907.

[2] If the volume occupied by ions is $v_1$ for short excitation and $v_2$ for long excitation, the ionic concentrations will be $n/v_1$ and $n/v_2$ respectively and the two intensities of phosphorescence will be proportional, $an^2/v_1$ and $an^2/v_2$. Prolonged excitation therefore produces an effect which is equivalent to a diminution in the coefficient of recombination.

teresis effects such as those exhibited in Fig. 40[1] are therefore to be expected.

If this explanation of hysteresis is correct the effect of the infra-red rays must be to facilitate the return of the substance to its normal condition: in other words to increase the rapidity of the diffusion by which the original distribution of the active material is restored. It is natural to expect such an effect in substances which are able to absorb the infra-red rays. But if the restoration is accomplished by the diffusion of neutral ions the rapidity of the action is surprising, for with strong infra-red rays we have found that an exposure of only a few seconds is sufficient to restore Sidot blende to its standard condition.[2]

### INFLUENCE OF IONIC GROUPING.

In discussing thermo-luminescence and the effect of infra-red rays upon phosphorescence Wiedemann and Schmidt[3] have suggested that some of the ions produced during excitation form semi-stable combinations or groups with the neutral molecules of the solvent, and that these groups may afterwards be broken down, and the ions liberated, by rise in temperature or by the absorption of infra-red rays. The formation of such groups as the result of ionization seems extremely probable, especially in the case of solids, and can scarcely fail to be of importance in any satifactory theory of phosphorescence. Introducing such additional hypotheses as are necessary to give definiteness to the suggestion of Wiedemann and Schmidt let us consider what the influence of such ionic groups will probably be.

We shall assume that the first effect of the exciting light is to produce dissociation in a part of the active material. The dissociation assumed may be either chemical or electrolytic;[4] and if of the

[1] PHYS. REV., Vol. 23, p. 41, 1906.

[2] Nichols and Merritt, PHYS. REV., Vol. 25, p. 362, 1906.

[3] Ann. der Phys., Vol. 56, p. 247, 1895.

[4] Since the electro-magnetic disturbance that constitutes light can get a hold on the molecules of the active material only by exerting forces upon the electrical charges in the molecule, and will always tend to separate the positive and negative parts, it appears probable that the first effect of the exciting light is always to produce some type of electrolytic dissociation, and that any chemical changes which may be exhibited are secondary effects.

latter type it may be either similar to the dissociation of ordinary electrolysis, or may consist of the expulsion from the molecule of one or more electrons, and thus resemble more closely the ionization of a gas by X-rays. For the sake of definiteness we shall assume that the effect of the exciting light is to produce such violent vibrations as to liberate a single electron from the molecule.

The two ions produced in this type of dissociation will differ greatly in mobility. The negative ion, owing to its small mass, will possess a velocity hundreds of times greater than that of the heavy positive ion, and in consequence will move about in the substance with considerable freedom. While the electrons will at times attach themselves to the molecules of the solid solvent this condition will usually be only temporary. We may assume in general that a constant fraction of the whole number of negative ions consists of electrons that are moving freely. The positive ions on the other hand will possess only a small mobility. While some of these ions will remain free, it is to be expected that many will attach themselves to molecules of the solvent or to undissociated molecules of the active substance. It is to be noted that the small velocity of the positive ions makes it probable that the groups formed by the union of a positive ion with a neutral molecule will be far more permanent than similar groups formed by the negative ion.

It will be seen that the collisions between positive and negative ions, which lead to the more or less gradual decay of the ionized condition after the exciting light has ceased to act, will be of three different kinds: (1) collisions between a negative ion and a free positive ion; (2) collisions between a negative ion and a positive ion that has attached itself to a neutral molecule of the solvent, and (3) collisions between a negative ion and a positive ion that is attached to a neutral molecule of the active substance. The number of modes of recombination may in fact be greater than three, since the positive ion may become the nucleus of more complicated molecular groups. We shall, however, restrict the discussion to cases in which there are only three modes of recombination.

When recombination occurs it is to be expected that vibrations will be set up in the resulting neutral molecule, and these vibrations, in

the theory here considered, are assumed to be the source of the light emitted during the phosphorescence. But the vibrations corresponding to the different modes of recombination will probably differ in violence, in frequency, and in radiating power.

Of the total number $n$ of positive ions at any time $t$ let $\varphi n$ be free, and $\psi n$ attached to neutral molecules of the active substance; then $(1-\varphi-\psi)n$ will be attached to molecules of the solvent. $\varphi$ and $\psi$ are proper fractions whose sum is less than unity, and which, in general, are functions of $t$, for the distribution of the positive ions will be subject to alteration during the decay of phosphorescence as well as during excitation. The number of recombinations between a free positive ion and an electron in unit time will be proportional to the number of free positive ions $\varphi n$, and to the number of free negative ions $n$, and may therefore be put equal $a_1\varphi n^2$, where $a_1$ is the coefficient of recombination. If the energy radiated as light due to one recombination is $p_1$ the intensity of the phosphorescence due to this mode of recombination will be

$$I_1 = p_1 a_1 \varphi n^2.$$

Similarly

$$I_2 = p_2 a_2 \psi n^2,$$

$$I_3 = p_3 a_3 (1-\varphi-\psi) n^2,$$

for the other two types of recombination.

The total phosphorescent light will thus consist of three parts. If the different modes of recombination give rise to vibrations of different frequency the phosphorescence spectrum will consist of three bands which decay at different rates, and which may differ widely in intensity.

The determination of the law of decay of phosphorescence upon the basis of the theory just outlined is thus seen to involve the determination of $n$, $\varphi$ and $\psi$ as functions of $t$. In the general case the solution presents difficulties that are well nigh insurmountable. The problem may be simplified, however, by an assumption, which, while doubtless not exactly true, probably gives in the majority of cases a close approximation to the actual conditions. It is assumed, namely, that $a_1 = a_2 = a_3$, in other words the probability that a collision will result in recombination is the same for the three types of collision. In this case

$$(1) \qquad \frac{dn}{dt} = -a\varphi n^2 - a\psi n^2 - a(1-\varphi-\psi)n^2 = -an^2,$$

$$(2) \qquad n = \frac{1}{1/n_0 + at},$$

where $n_0$ is the number of positive (or negative) ions when excitation ceases.

To determine $\varphi$ and $\psi$ as functions of $t$ it is necessary to make some assumption regarding the rate at which the free positive ions attach themselves to neutral molecules. Since the number of neutral molecules is presumably large as compared with the number of ions, it is reasonable to assume that the rate at which new groups are formed is proportional to the number of ions that are still free to enter into such combination. In other words we may assume $k_1\varphi n$ and $k_2\varphi n$ as the rates of formation of new groups of the two possible types. Since the positive ions, whether free or attached, are also recombining with the negative ions we have

$$(3) \qquad \frac{d}{dt}(\varphi n) = -a\varphi n^2 - (k_1 + k_2)\varphi n.$$

While positive ions will occasionally break loose from the groups to which they have attached themselves and return to the "free" condition, this will occur only rarely on account of the sluggishness with which these ions move. I have therefore omitted as negligibly small the positive term due to this cause which should appear in the right hand member of equation (3). At high temperatures, however, and perhaps under other special conditions, the omision of this term will no longer be permissible. If the molecular movements are sufficiently violent, due to high temperature or other causes, the formation of groups may even be prevented altogether. Such cases will be considered later.

Equation (3) may be written

$$\frac{d}{dt}(\varphi n) = \varphi\frac{dn}{dt} + n\frac{d\varphi}{dt} = -a\varphi n^2 - (k_1 + k_2)\varphi n.$$

Remembering that $dn/dt = -an^2$ this becomes

$$\frac{d\varphi}{dt} = -(k_1 + k_2)\varphi,$$

$$\varphi = \varphi_0 e^{-mt},$$

where $m = k_1 + k_2$ and $\varphi_0$ is the value of $\varphi$ for $t = 0$.

In the case of the positive ions that are attached to neutral molecules of the active substance recombinations are occurring with negative ions at the rate $a\psi n^2$, while new groups are being formed by the attachment of free positive ions at the rate $k_1\varphi n$

$$\therefore \frac{d}{dt}(\psi n) = -a\psi n^2 + k_1\varphi n$$

or

$$\psi\frac{dn}{dt} + n\frac{d\psi}{dt} = -a\psi n^2 + k_1\varphi n. \tag{5}$$

Since

$$\frac{dn}{dt} = -an^2$$

we have

$$\frac{d\psi}{dt} = k_1\varphi = k_1\varphi_0 e^{-mt},$$

$$\therefore \psi = -\frac{k_1\varphi_0}{m}e^{-mt} + \text{const.}$$

Putting $\psi_0$ for the value of $\psi$ when $t = 0$

$$\psi = \psi_0 + \frac{k_1\varphi_0}{m}(1 - e^{-mt}). \tag{6}$$

For the intensities of the three constituents of the phosphorescent light we have therefore

$$I_1 = p_1 a\varphi n^2 = \frac{p_1 a\varphi_0 e^{-mt}}{(1/n_0 + at)^2},$$

$$I_2 = p_2 a\psi n^2 = \frac{p_2 a[\psi_0 + k_1\varphi_0/m(1 - e^{-mt})]}{(1/n_0 + at)^2},$$

$$I_3 = p_3 a(1 - \varphi - \psi)n^2 = \frac{p_3 a[1 - \psi_0 - k_1\varphi_0/m - k_2\varphi_0/m \cdot e^{-mt})]}{(1/n_0 + at)^2}.$$

Since we have usually plotted the reciprocal square root of the intensity of phosphorescence it will be convenient to use the same procedure here.

$$1/\sqrt{I_1} = \frac{1}{\sqrt{p_1 a\varphi_0}}e^{\frac{1}{2}mt}(1/n_0 + at),$$

$$1/\sqrt{I_2} = \frac{1/n_0 + at}{\sqrt{p_2 a[\psi_0 + k_1\varphi_0/m(1 - e^{-mt})]}},$$

$$1/\sqrt{I_3} = \frac{1/n_0 + at}{\sqrt{p_3 a[1 - \psi_0 - k_1\varphi_0/m - k\varphi_0/m \cdot e^{-mt}]}}.$$

Replacing certain groups of constant terms by single letters for brevity these expressions may be written

$$1/\sqrt{I_1} = A_1\varepsilon^{\frac{1}{2}mt}(1/n_0 + at),$$

$$1/\sqrt{I_2} = \frac{1/n_0 + at}{\sqrt{A_2 - B_2e^{-mt}}},$$

$$1/\sqrt{I_3} = \frac{1/n_0 + at}{\sqrt{A_3 - B_3e^{-mt}}}.$$

If a curve is plotted for $1/\sqrt{I_1}$ in accordance with the above equation it is found to be of the type shown in Fig. 72 for $\gamma = 0$. The curve for $1/\sqrt{I_2}$ and $1/\sqrt{I_2}$ is concave *upward* during the early stages of decay, becoming practically straight when $t$ is so large as to make $e^{-mt}$ inappreciable.

No decay curves corresponding to either of these types has been observed. It must be remembered, however, that the effects of absorption, diffusion, and irregular distribution have been neglected in the present discussion. It is probable that one or more of these sources of disturbance are present, in which case the theoretical decay curves would be modified in such a way as to make them correspond more nearly with the curves actually observed. If $m$ is large, for example, the curve for $I_2^{-\frac{1}{2}}$ will be straight except in the immediate neighborhood of $t = 0$. Irregularities in the distribution of the active substance would then produce a deviation from linearity, as discussed on pp. 377–381. It appears to me probable that the observed facts, in the cases of phosporescence thus far studied, are best explained in this way. It is interesting to note, however, that curves may be obtained as the result of ionic grouping which agree very closely with the experimental curves, even on the assumption of a uniform distribution of the active material. If, for example, $I_1$ and $I_2$ *both* contribute to the phosphorescence, while $I_3$ is zero or negligible

$$I = I_1 + I_2 = \frac{p_2 a[\psi_0 + k_1\varphi_0/m \cdot (1 - e^{-mt})] + p_1 a\varphi_0 e^{-mt}}{(1/n_0 + at)^2},$$

$$(7) \qquad 1/\sqrt{I} = \frac{1/n_0 + at}{\sqrt{A + Be^{-mt}}},$$

where

$$A = p_2 a\left(\psi_0 + \frac{k_1\varphi_0}{m}\right),$$

$$B = p_1 a\varphi_0 - p_2 a\frac{k_1\varphi_0}{m}.$$

In case all three modes of recombination contribute to the phosphorescence we obtain a similar expression for $I^{-\frac{1}{2}}$ except that $A$ and $B$ now have the values

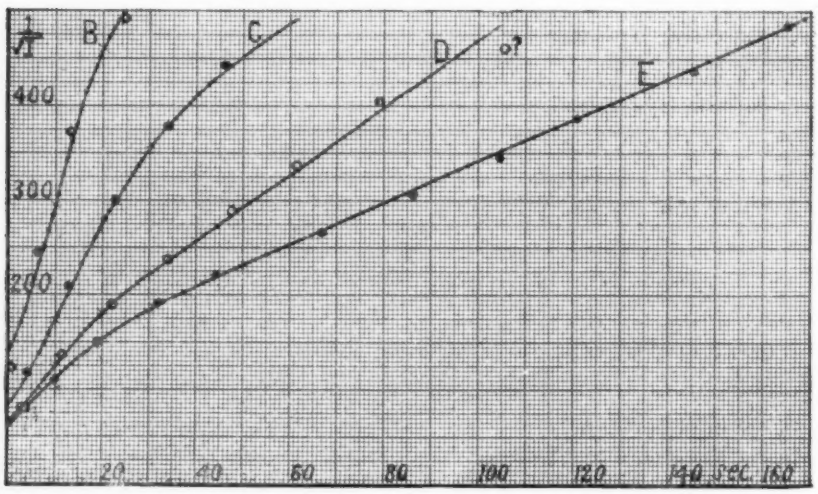


Fig. 71. Observed decay curves for different durations of excitation compared with curves computed from the equation

$$\frac{1}{\sqrt{I}} = \frac{1/n_1 + at}{\sqrt{B(\gamma + e^{-mt})}}.$$

The times of excitation and the relative numerical values of the constants used in computation are as follows:

| Curve. | Excitation. | $\gamma$ | $1/N_0$ | $\sqrt{B}$ | |
|---|---|---|---|---|---|
| $E$ | 60 sec. | 0.36 | 72 | 1 | |
| $D$ | 37 " | 0.4 | 167 | 2.18 | $a = 4.8$ |
| $C$ | 11.6 " | 0.1 | 336 | 4 | $m = 0.16$ |
| $B$ | 5.4 " | 0.1 | 650 | 4.35 | |

$$A = p_2\alpha\left(\varphi_0 + \frac{k_1\varphi_0}{m}\right) + p_1\alpha\left(1 - \varphi_0 - \frac{k_1\varphi_0}{m}\right),$$

$$B = p_1\alpha\varphi_0 - p_2\alpha\frac{k_1\varphi_0}{m} - p_3\alpha\frac{k_2\varphi_0}{m}.$$

In Fig. 71 several curves have been plotted for $I^{-\frac{1}{2}}$ by means of this equation. Values of the constants have been determined by trial so as to make these curves correspond as nearly as possible with the series of experimental curves obtained with Sidot blende by varying the time of excitation.[1] Observational points are indicated by circles. It will be seen that, except in the case of one curve, the agreement is highly satisfactory.

To give an idea of the character of the decay curves which might result from the presence of grouped ions (disturbances due to diffusion, absorption, etc., being neglected) we may write equation (7) in the form

$$\frac{1}{\sqrt{I}} = \frac{1/n_0 + at}{\sqrt{B}} \cdot \frac{1}{\sqrt{\gamma + e^{-mt}}} = \frac{(1/n_0 + at)}{\sqrt{B}} T,$$

where

$$T = \frac{1}{\sqrt{\gamma + e^{-mt}}} \quad \text{and} \quad \gamma = A/B.$$

The first factor alone plots as a straight line. The deviation from linearity in the curve for $I^{-\frac{1}{2}}$ is therefore determined by the second factor $T$. Putting $m = 1$ I have computed $T$ as a function of $t$ for several values of $\gamma$, the results being plotted in Fig. 72. For values of $\gamma$ ranging from 0.1 to 5.0 the curves are of such a character as to correspond with the experimental curves for $I^{-\frac{1}{2}}$. But for smaller values of $\gamma$ a double curvature is shown which is not found in any

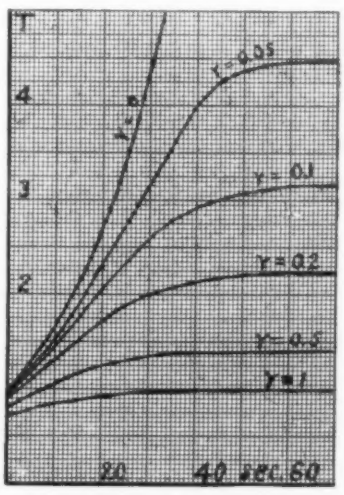


Fig. 72. Curves showing the relation between $T$ and $t$ for different values of $\gamma$ where

$$T = \frac{1}{\sqrt{\gamma + e^{-t}}}.$$

[1] Nichols and Merritt, PHYSICAL REVIEW, Vol. 23, p. 45, Fig. 44.

of the curves that we have determined. There is, however, an indication of such a double curvature in some of the results of Pierce. It is clear that disturbances, due, for example, to irregularities in the distribution of the active material, might so alter the early part of the curve as to eliminate any peculiarities of this nature. In fact there is at present so much uncertainty regarding the relative importance of the different factors that influence the form of the curve for small values of $t$ that it is difficult to reach any definite conclusions concerning this part of the curve. Experiments bearing upon the distribution of the active material, the rate of diffusion of the ions, and related matters are greatly needed.

### Hysteresis, Temperature Effects, Etc., Explained by Ionic Grouping.

To account for the hysteresis exhibited by phosphorescent substances, in other words, the effect of a previous exposure upon the phosphorescence produced by a given excitation, it is necessary to consider the essential difference that probably exists between the groups formed by the union of positive ions with neutral molecules of the active substance and those formed by the attachment of positive ions with molecules of the solvent. For the sake of brevity, as well as for reasons that will appear shortly, we shall refer to the former as *favorable groups* and to the latter as *unfavorable groups*.

We have already introduced the assumption that light is produced by the recombination of a negative ion with a favorable group, while the recombination of the unfavorable groups, at least in some cases, gives out no light. A difference is to be expected also in the behavior of the neutral molecules that result from recombination in the two cases. A favorable group consists in a positive ion attached to at least one neutral molecule *of the same sort.* It seems natural to expect that forces similar to those that hold together the molecules of a crystal may cause this grouping to persist even after recombination has occurred. In the case of the unfavorable groups this tendency to persist can scarcely be present in the same degree if at all.

The condition of the phosphorescent substance is thus different after phosphorescence has ceased from what it was before excita-

tion. The difference consists in the presence in the mass of a larger number of grouped molecules of the active substance, which are so intimately connected that when one member of the group is dissociated during subsequent excitation its positive ion is in a position to form immediately one of the groups favorable to phosphorescence. After the substance has been excited it is therefore in a condition which enables a subsequent excitation to produce a larger proportion of favorable groups than would be produced by a similar excitation of the fresh substance. In other words the $\psi_0$ of equation (7) is increased.

During excitation we have dissociation and recombination taking place at the same time; and the recombinations that occur during excitation will bring about the same change in the condition of the substance that we have assumed during decay. The value of $\psi_0$ will therefore increase with the duration of exposure to the exciting rays. Prolonged excitation, up to the point where saturation is reached, also increases the number of ions, *i. e.*, the value of $n_0$. A series of decay curves for different times of exposure should therefore resemble the curves of Fig. 71, which are computed from equation (7) by giving progressively increasing values to the constants $\psi_0$ and $n_0$.

The new condition in which a substance is left after phosphorescence can scarcely be one of complete stability. The natural and stable arrangement of the molecules is that of the substance before it has been disturbed by the action of light. It is to be expected, therefore, that there will be a more or less gradual return to the normal state after the light has ceased to act. The recombination of the ions produced by excitation, with the accompanying phosphorescence, forms only one stage in the complete return to the normal state, and is followed by a more gradual breaking down of the molecular groups resulting from recombination. We thus have an explanation of the effect of rest. The effect of exposure to infra-red rays and of elevation of temperature is to hasten the return to the normal state by increasing the rate at which these groups disintegrate.

To account for the action of the infra-red rays during excitation and decay it is only necessary to assume that these rays also have

the power of breaking down the "favorable groups." In the case of Sidot blende the effect on the unfavorable groups appears to be inappreciable. Upon exposure to infra-red during decay the first result is to diminish the number of favorable groups, and to correspondingly increase the number of free positive ions. This, by itself, will not greatly alter the intensity of phosphorescence; for in the phosphorescence of Sidot blende the recombination of a free positive ion appears to be nearly or quite as effective as the recombination of a favorable group. But an increase in the number of free ions causes an increase in the rate at which unfavorable groups are formed. The positive ions that are shaken loose from the favorable groups therefore pass quickly into the inactive condition, and a rapid diminution in the intensity of phosphorescence results. The rate of decrease of course depends upon the intensity of the active rays.

If the infra-red rays are allowed to act for a short time and are then cut off, the condition of the phosphorescent substance will differ in two respects from that which it would have reached during ordinary decay: (1) the number of favorable groups is less than it would have been without the action of the longer waves; (2) the number of free ions is, at least to some extent, in excess of the normal. After the infra-red rays have ceased to act, however, the free ions will soon form groups again, either favorable or unfavorable, and the decay curve will quickly return to the standard form. But the number of favorable groups will be less than if the infra-red rays had not acted. The effect of exposure to the longer waves is simply to bring the substance quickly into the same condition that it would ordinarily acquire only after a much longer period of decay. The theory here discussed is thus seen to be incomplete agreement with the experimental results shown in Figs. 60 and 61 of the eighth article of this series.[1]

It seems probable that in some substances certain rays, presumably in the infra-red, may have the effect of breaking down the unfavorable as well as the favorable groups. In such cases exposure to these rays would probably bring about an increase in the brilliancy of phosphorescence instead of a decrease. This is said to be

[1] PHYS. REV., Vol. 25, p. 371.

the case with certain of the phosphorescent sulphides. The same effect would be produced in substances where the recombination of a free positive ion gives out more light than that of an attached ion ; *i. e.*, where $p_1 > p_2$.

In cases like that of Sidot blende the form of the decay curve as modified by exposure to infra-red rays may be determined as follows :

We shall assume that the rate at which favorable groups are broken down is proportional to the intensity of the active rays $I_r$ and the number of favorable groups present ($\psi n$). We therefore have

$$\frac{d}{dt}(\psi n) = -\alpha\psi n^2 - R\psi n + k_1\varphi n \tag{8}$$

where $R$ is proportional to $I_r$.

The destructive effect of the infra-red is so great, even for rays of small intensity, while $k_1$ is so small, that the last term $k_1\varphi n$ may in general be neglected. It is only in the case of exposure to very weak rays, or with substances which show the infra-red effect in small intensity, that the omission of this term will lead to appreciable errors. Equation (8) therefore becomes

$$\psi\frac{dn}{dt} + n\frac{d\psi}{dt} = -\alpha\psi n^2 + n\frac{d\psi}{dt} = -\alpha\psi n^2 - R\psi n,$$

$$\frac{d\psi}{dn} = -R\psi,$$

$$\psi = \psi_1\epsilon^{-Rt}; \tag{9}$$

$t$ is here reckoned from the time when exposure to the infra-red rays begins. If we take $t$ as the time that has elapsed since the end of excitation we have

$$\psi = \psi_1 e^{-R(t-t_1)}$$

where $t_1$ is the time at which the longer waves begin to act and $\psi_1$ is the value of $\psi$ at this time.

To determine the number of free positive ions $\varphi n$ after the infra-red rays begin to act we have the equation

$$\frac{d}{dt}(\varphi n) = -a\varphi n^2 + R\psi n - k_2\varphi n,$$

$$\varphi\frac{dn}{dt} + n\frac{d\varphi}{dt} = -\varphi an^2 + n\frac{d\varphi}{dt} = -a\varphi n^2 + R\psi n - k_2\varphi n,$$

$$\frac{d\varphi}{dt} + k_2\varphi = R\psi = R\psi_1 e^{-Rt},$$

$$\varphi = \varphi_1 e^{-k_2(t-t_1)} - \frac{R\psi_1}{k_2 - R}e^{-R(t-t_1)}. \tag{10}$$

An interesting special case, corresponding to the experimental conditions in much of our work with Sidot blende, is that in which the exposure to infra-red rays begins at once when excitation ceases, *i. e.*, $t_1 = 0$. In this case

$$\varphi_1 = \varphi_0, \quad \psi_1 = \psi_0, \quad \varphi = \varphi_0 e^{-k_2 t} + \frac{R\psi_0}{k_2 - R}(e^{-Rt} - e^{-k_2 t}), \quad \psi = \psi_0 e^{-Rt},$$

$$I = p_1 a\varphi n^2 + p_2 a_2 \psi n^2 = (A_1 e^{-Rt} + B_1 e^{-k_2 t})n^2,$$

where

$$A_1 = p_2 a_2 \psi_0 \frac{k_2}{k_2 - R}, \quad B_1 = p_1 a_1 \left(\varphi_0 - \frac{R\psi_0}{k_2 - R}\right).$$

For the special case where $p_1 a_1 = p_2 a_2$,

$$\frac{1}{\sqrt{I}} = \eta = \frac{1/n_0 + at}{\sqrt{\dfrac{\psi_0 k_2}{k_2 - R}e^{-Rt} + \left(\varphi_0 - \dfrac{R\psi_0}{k_2 - R}\right)e^{-k_2 t}}}.$$

If the infra-red rays are intense so that $R/k_2$ is large,

$$\frac{1}{\sqrt{I}} = \frac{1/n_0 + at}{\sqrt{k_2\psi_0/R \cdot e^{-Rt} + (\psi_1 + \psi_0)e^{-k_2 t}}},$$

and in the extreme case where $R$ may be treated as infinite

$$\frac{1}{\sqrt{I}} = \frac{1/n_0 + at}{\sqrt{(\varphi_0 + \psi_0)e^{-k_2 t}}}.$$

This gives a curve having the same form as the observational curve shown in Fig. 64, which is reproduced from the preceding article of this series. The data of Figs. 65, 66 and 67[1] will be found to give curves of the same form for $1/\sqrt{I'}$, but the curve has been plotted only in the case of Fig. 64.

[1] PHYS. REV., Vol. 25, p. 362.

At high temperatures the increased activity of the molecular movements will tend to prevent the formation of groups, or rather to destroy the groups almost as quickly as they are formed. All those phenomena that depend upon the existence of groups will therefore become less prominent as the temperature rises. Sooner or later a temperature will be reached where groups can no longer

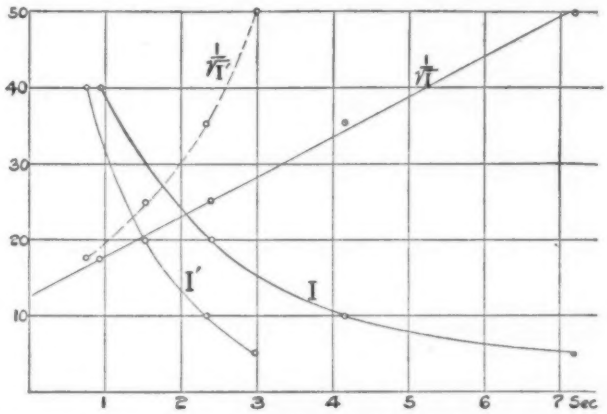


Fig. 64. Decay curves with and without infra-red. $\lambda = 0.546\,\mu$.

exist. At temperatures above this point we should expect no effect from exposure to the infra-red, and all hysteresis effects should disappear. The experiments of Pierce show that hysteresis still persists in Balman's paint at 133° C. No other data bearing upon this point are available.

It would be a matter of no great difficulty to develop the theory of ionic groups in much greater detail than has here been attempted, for when uncomplicated by the effects of irregular distribution and diffusion the theory lends itself readily to analytical treatment. But in view of the small amount of experimental data that are available for testing the conclusions it seems inadvisable to carry the development further at present.

## Summary.

In the case of a homogeneous substance having only one band in its phosphorescence spectrum and uniformly excited throughout, the dissociation theory first suggested by Wiedemann and Schmidt leads to a linear relation between $t$ and $I^{-\frac{1}{2}}$ during the decay of

phosphorescence.[1] The observed decay curve, however — *i. e.*, the curve obtained when $I^{-\frac{1}{2}}$ is plotted as a function of $t$ — usually shows a more or less sharp curvature in the early stages of decay, and only later becomes straight. Using the dissociation theory as a basis the present paper discusses first the influence upon the decay curve of various disturbing factors, such as absorption of the exciting and emitted light, diffusion, etc. The paper then discusses the effect upon the various phenomena of phosphorescence of the formation of complex ions, which are assumed to be produced by the attachment of simple ions to neutral molecules; and after the introduction of certain hypotheses regarding the behavior of such ionic groups, an analytical theory is developed.

Briefly the results of the discussion are as follows:

1. Data thus far obtained for the decay of phosphorescence in no case definitely contradict Becquerel's explanation of the form of the decay curve, viz., that the curvature is due to the existence of two bands in the phosphorescence spectrum. Several objections to this explanation are, however, mentioned. For example, the fact that the decay curve has the usual form even when precautions are taken to study only a single band; the fact that the decay curve is of the same type for all substances thus far studied; and the fact that Becquerel's explanation takes no account of hysteresis phenomena, the effect of infra-red rays, etc.

2. It is shown that lack of transparency in the phosphorescent substance, resulting in the absorption of either the exciting light or the emitted light or both, will cause a slight curvature in the decay curve. But the effect can under no circumstances be sufficient to account for the observed deviation from linearity.

3. Lack of uniformity in the distribution of the active material throughout the mass of the phosphorescent substance will cause a deviation from linearity corresponding to that actually observed. Under certain conditions the effect is the same as though the substance possessed two or more bands, coincident as regards wavelength, but differing in rate of decay. It is pointed out that such a lack of homogeneity is to be expected from the method of preparation of phosphorescent substances, and has a great deal to do with the complexity of the phenomena.

[1] Nichols and Merritt, PHYS. REV., Vol. 22, p. 279, 1906.

4. Diffusion of the ions will produce effects similar to those caused by irregularities in the distribution of the active material without diffusion, but the effects will be more marked. An explanation of hysteresis effects may also be based upon the presence of diffusion.

5. The assumption of complex or grouped ions is shown to lead to a law of decay which agrees closely with experiment. Ionic grouping also accounts satisfactorily for the dependence of the decay curve upon the duration of excitation and the previous history of the substance, and for the effect of exposure to the infra-red.

The preceding discussion appears to justify the conclusion that the dissociation theory proposed by Wiedemann and Schmidt is able to account satisfactorily for all the phenomena of phosphorescence thus far studied. Additional quantitative data are greatly needed, however, in order to make possible the further development of the theory. The present difficulty is not so much in accounting for the observed facts as in discriminating between different hypotheses that are at present equally plausible, and in deciding to what extent various recognized sources of disturbance are of importance. The form of the decay curve, for example, may be accounted for equally well by the assumption of two bands, by an irregular distribution of the active substance, by diffusion, or by ionic grouping, and is unquestionably modified by absorption. No quantitative test of either explanation is possible until the relative importance of the other factors is known. It may be, for instance, that diffusion does not occur at all; and it is possible, but not probable, that the disturbances due to lack of homogeneity are of no significance. Experiments that will furnish a definite answer to questions of this sort are of the greatest importance in the development of this or any other theory of phosphorescence.

# ON THE CHARGES GAINED BY INSULATED METALLIC CONDUCTORS SURROUNDED BY OTHER CONDUCTORS AND THE RELATION OF THESE CHARGES TO THE VOLTA EFFECT.[1]

BY J. K. ROBERTSON, M.A.

## I. INTRODUCTION.

IN 1903 McLennan and Burton[2] found that a metal cylinder, either of lead, copper, zinc, tin or aluminium, placed within, and insulated from an outer earthed one of the same material gradually acquired a negative charge, the value of which steadily rose to a maximum which varied with the metal. In November, 1907, McKeon[3] published results of experiments made concerning the same effect, which are not altogether in agreement with those observed by McLennan and Burton. He found, in the case of lead and tin receivers, that the charge acquired was positive. Further, while the observations of McLennan and Burton extended only over a period of some hours, his were continued for several days. During such an interval, moreover, he observed variations in the value of the charge. From his observations he concluded that these changes took place at definite periods of the day, and, in explanation, suggested a connection between them and the diurnal variations in the ionization of atmospheric air to which attention has been drawn by Campbell and Wood[4] and others.

In view of the lack of agreement existing between the two sets of observations, the writer undertook to make a closer examination of the effect in order to ascertain, (1) its cause, and (2) its relation to variations in the earth's penetrating radiation and to the daily changes in the ionization of the atmosphere noted above.

[1] Communicated by Prof. J. C. McLennan.
[2] Phil. Mag., September, 1903.
[3] PHYS. REV., November, 1907.
[4] Phil. Mag., February, 1907.

On making a rather exhaustive set of observations with different metals, it was found that the sign of the charge acquired by the insulated cylinder varied largely with the treatment to which the surfaces of the outer and inner cylinders were subjected. For example, it was found possible, with two particular pairs of cylinders, to alter the sign of the charge merely by thoroughly cleaning the surfaces. A summary of the results obtained in a variety of cases is given in Table I. (p. 404) and it will be seen from it that a close connection exists between the surface condition and the nature of the charge acquired.

Variations with time in the magnitude of the charge were also observed in a number of cases, but these, in so far as the observations extended, were not such as to indicate any marked periodicity. In only one case, that of lead no. 1 in lead no. 2, were observations made for a very extended period of time, and the resulting curve (vide Fig. 1) although showing marked variations would hardly indicate the presence of definite periodic changes.

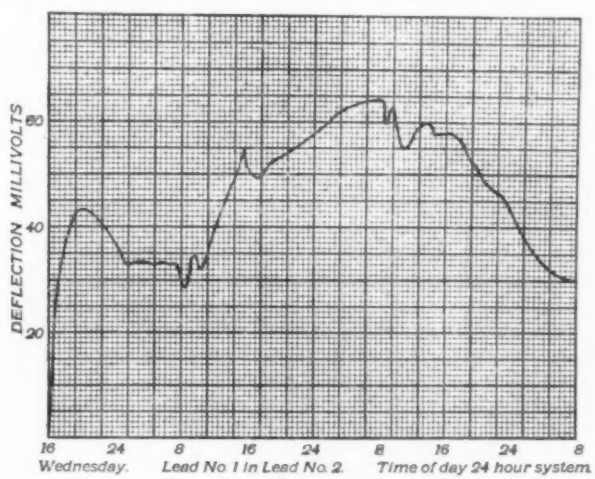


Fig. 1.

Throughout the investigation the Volta effect seemed to be of considerable importance, so much so that the writer was led to undertake a series of experiments to determine, if possible, by a somewhat similar method, the contact potential difference between two metals. A few measurements have been made, and these seem

to indicate that, in this latter investigation at any rate, secondary radiation is a very important factor in modifying results arising from the Volta effect.

## II. EXPERIMENTS — METAL EFFECT.

In carrying out the investigation, an attempt was made to examine as many combinations of cylinders as possible, and use was made of the following materials: (1) four outer and two inner cylinders of lead. These were made of lead selected at random from different sheets taken from stock of the laboratory workshop; (2) two outer and two inner ones of tin, all made out of the same sheet of the substance; (3) an outer and an inner of zinc, made from two entirely different sheets of the metal.

An effort was also made to ascertain, if possible, the connection between the surface condition of the metals and the sign and nature of the charge gained by the inner cylinder. To accomplish this, cylinders were washed with different solutions and abraded to a greater or less extent with emery paper. Sets of observations were also taken with cylinders coated with aluminium and with bronze paints.

The outer cylinders were about 60 cm. long and 25 cm. in diameter, the inner ones two or three centimeters shorter and about 15 cm. in diameter. Larger ones were made in one or two cases, by joining two outer ones and two inner ones together, so as to ascertain in this way the effect of varying the size of the cylinders.

*Method of Experimenting.* — The method of measuring the charge was essentially the same as that employed by the previous investigators. The inner cylinder was insulated from the outer by means of paraffin blocks, and the charge acquired measured by a sensitive quadrant electrometer. Connection was made as shown in Fig. 2. The lid at one end of the outer cylinder had a cylindrical projection of the same material, which was inserted into a box lined with tin foil. This box contained the special arrangement devised by Professor McLennan[1] for making and breaking the earth connection of one pair of quadrants without altering the capacity of the system. To one end of the inner cylinder was soldered a piece of

[1] PHYS. REV., March, 1905.

metal of the same material, which also projected into the box, and was joined to the "make and break." The inner cylinder and all wires connecting it to the electrometer were screened from electrostatic disturbances by means of earthed conductors.

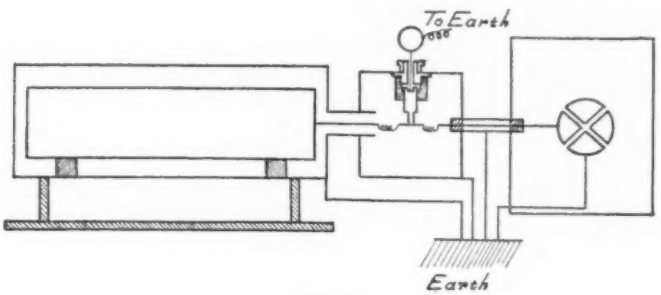


Fig. 2.

The electrometer used was of the Dolezalek type, the quadrants being insulated with ebonite supports, and it had a sensibility such that for a potential of one volt it gave a deflection of about 600 mm. on a scale about one meter from the needle. A few readings were taken with another instrument of the same type with amber supports. No difference was observed, however, between the results obtained with the two instruments.

The chief difference between this arrangement and that of the previous investigators lay in the fact that they used air-tight receivers, while those of the writer were not hermetically sealed. This is of some importance, as it has been shown [1] that the conductivity of air enclosed in a metallic receiver gradually increases with the time it is confined. Meteorological conditions might also have a disturbing influence.

## III. Discussion of Results.

(*a*) *Change of Sign of Charge Acquired by the Insulated Cylinder.* — A glance at Table I. will show the great variation observed in the sign of the charge acquired by the respective insulated cylinders. Even with a selected combination of cylinders, the sign acquired was not always found to be the same, for, in some cases, it was possible to reverse the sign by simply cleaning the metals. Lead no. 1

[1] McLennan & Burton, Phys. Rev., Vol. XVI., No. 3, 1903.

TABLE I.

| No. | Combination. | Sign of Charge of Insulated Cylinder. | Maximum and Minimum Values of Potential of Insulated Cylinder in Millivolts. | Remarks. |
|---|---|---|---|---|
| 1 | Lead no. 1 in no. 2 | + | 102 approx. | Needle positive |
| 2 | do | + | 113 | Needle negative. Same day as no. 1 |
| 3 | do | + | 79, 72, 78 | Needle positive. Radium used. Four days after no. 1 |
| 4 | do | − | 46, 32 | After cleaning. Radium used, needle positive |
| 5 | do | − | 45, 41 approx. | Needle negative. Radium used |
| 6 | do | − | 31.8 | One day after no. 4 |
| 7 | do | − | 29 approx. | Radium inside inner cylinder. One day after no. 6 |
| 8 | do | − | 27, 24, 25 | Four days after no. 4. Radium used |
| 9 | do | − | 13 | Twenty days after no. 4 |
| 10 | Lead no. 1 in no. 1 | + | 84.6, 83, 31 | Fourteen days after no. 4. Outer no. 1 had not been cleaned for some months |
| 11 | Lead no. 1 in no. 3 | + | 59, 58, 55 | Radium used but removed between the values 58 and 55 |
| 12 | do | + | 22, 9 | Radium used. Lead no. 1 had been cleaned about 7 days |
| 13 | do | + | 42.5, 41 | Fourteen days after no. 12 |
| 14 | Lead no. 2 in no. 3 | − | 50 | Radium used, inner cylinder had been abraded with emery paper |
| 15 | Double combination. Lead no. 1 in lead no. 2. Lead no. 2 in lead no. 3 | − | 27.2, 21 | Radium used. Eleven days after no. 4, and four days after no. 14 |
| 16 | do | − | 13, 5 | Two days after no. 15 |
| 17 | Lead no. 2 in no. 4 | + | 174, 160 | Cleaned one day before |
| 18 | do | − | 268.7 | One day after no. 17 |
| 19 | do | + | 105, 70 | Three days after no. 17 |
| 20 | do | + | 105, 70 | Five days after no. 17 |
| 21 | do | + | 105, 70 | Six days after no. 17 |
| 22 | Lead coated with aluminium paint. No. 2 in no. 4 | − | 22.6 | |
| 23 | Same combination plus two coats of bronze paint | + | 75 | |
| 24 | do | + | 125 | One day after no. 23 |
| 25 | Tin no. 1 in tin no. 1 | − | 83, 66, 85 | |

TABLE I. — *Continued.*

| No. | Combination. | Sign of Charge of Insulated Cylinder. | Maximum and Minimum Values of Potential of Insulated Cylinder in Millivolts. | Remarks. |
|---|---|---|---|---|
| 26 | Tin no. 2 in tin no. 2 | − | 91, 48, 89 | Nos. 1 and nos. 2 were made out of the same sheet of tin |
| 27 | Double combination. Tin no. 1 + tin no. 2 in tin no. 1 + tin no. 2 | − | 94 | Two days after no. 26 |
| 28 | Tin no. 2 in tin no. 2 | + | 171, 38 | After cleaning |
| 29 | do | + | 82 | One day after no. 28 |
| 30 | Tin no. 1 in tin no. 1 both coated with aluminium paint | − | 162 | Eleven days after no. 25 |
| 31 | do | − | 156, 155 | One day after no. 30 |
| 32 | Same combination coated with tinfoil. | − | 36.4, 25.5 | |
| 33 | do | − | 27.2 | One day after no. 32 |
| 34 | Same combination with tinfoil scraped off | − | 76, 60 | |
| 35 | Combination no. 34 plus a coat of bronze | − | 91, 66 | Five days after no. 34. At first a small positive charge indicated |
| 36 | do | − | 103 | Two days after no. 35. At first a small positive charge |
| 37 | Zinc in zinc | + | 92, 51 | Cleaned before using. The inner and outer cylinders were not ou of same sheet |
| 38 | Zinc in zinc, both covered with one coat of aluminium paint | + | 189, 175 | Two days after no. 37 |
| 39 | Zinc in zinc, both coated with two coats of aluminium paint | − | Off the scale, 475 | Three days after no. 38 |
| 40 | do | − | Off the scale, 740 | Four days after no. 39 |

in lead no. 2 (vide Table I., nos. 3 and 4) changed from positive to negative, after the cylinders had been thoroughly cleaned by being abraded with emery paper, and then washed with distilled water, dilute hydrochloric acid, water, ammonia, water and alcohol. On

the other hand, tin no. 2 in tin no. 2 was reversed from negative to positive, after being washed in the same manner (vide Table I., nos. 26, 28, and 29).

In all cases where the inner and outer cylinders were known to be of the same composition, namely, tin no. 1, tin no. 2, and tin no.

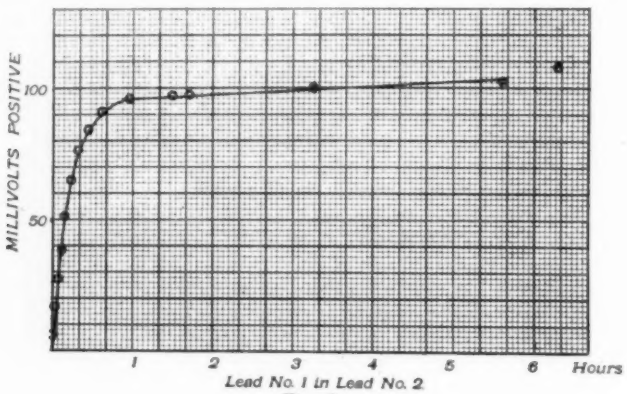

Fig. 3.

1, with its various coats of paint, with the single exception of the cleaned tin, the sign was negative. Whenever the outer and inner cylinders were not of exactly the same material, there would be a

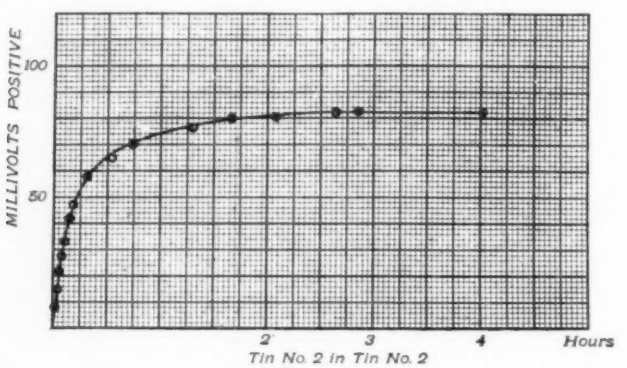

Fig. 4.

contact potential difference, and in all such cases this would be an important factor in determining the nature of the charge acquired. Assuming that there was a negative effect due to another cause, this Volta effect would explain the variations in the sign for many other combinations, and also for the change from positive to negative of

the lead combination after cleaning. It would not, however, explain the change from negative to positive of the tin combination after cleaning, unless, indeed, we are to suppose that it was possible to

TABLE II.

*Lead No. 1 in Lead No. 2. Without Radium.*

| Time. | Deflection (in Millivolts). | Time. | Deflection (in Millivolts). |
|---|---|---|---|
| 50 sec. | 6 positive | 19 min. 45 sec. | 76 positive |
| 1 min. 20 " | 11 " | 26 " 50 " | 84 " |
| 2 " 15 " | 17 " | 36 " 45 " | 91 " |
| 2 " 55 " | 21 " | 58 " 15 " | 96 " |
| 4 " 8 " | 27 " | 79 " 10 " | 96 " |
| 4 " 52 " | 32 " | 1 hr. 30 " | 97 " |
| 6 " 5 " | 38 " | 1 " 43 " | 97 " |
| 7 " 5 " | 42 " | 3 " 16 " | 100 " |
| 9 " 7 " | 51 " | 5 " 37 " | 102 " |
| 11 " 5 " | 57 " | 6 " 18 " | 108 " |
| 14 " 10 " | 65 " | 18 " 22 " | 113 " |

select two pieces of tin from the same sheet which differed in constitution and structure sufficient to exhibit a contact difference of potential. It would also not explain the different sign of lead no. 2 in lead no. 4 (vide Table I., nos. 17 and 18) on two successive days, nor the change from negative to positive, when, to the same combination of cylinders coated with aluminium paint, was added two coats of bronze (vide Table I., nos. 22 and 23).

TABLE III.

*Lead No. 1 in Lead No. 2. With Radium.*

| Time. | Deflection (in Millivolts). | Time. | Deflection (in Millivolts). |
|---|---|---|---|
| 8 sec. | 41 positive | 1 hr. 33 min. | 75 positive |
| 12 " | 61 " | 1 " 50 " | 75 " |
| 15 " | 67 " | 2 " 13 " | 74 " |
| 20 " | 69 " | 3 " 15 " | 74 " |
| 30 " | 77 " | 3 " 58 " | 72 " |
| 3½ min. | 79 " | 4 " 10 " | 75 " |
| 14 " | 79 " | 4 " 22 " | 76 " |
| 35 " | 78 " | 4 " 33 " | 78 " |
| 46 " | 77 " | 4 " 43 " | 78 " |
| 66 " | 76 " | | |

In the case of the tin combination coated with aluminium and with bronze paints, at first a small positive charge was observed, which slowly changed into a comparatively large negative one. This

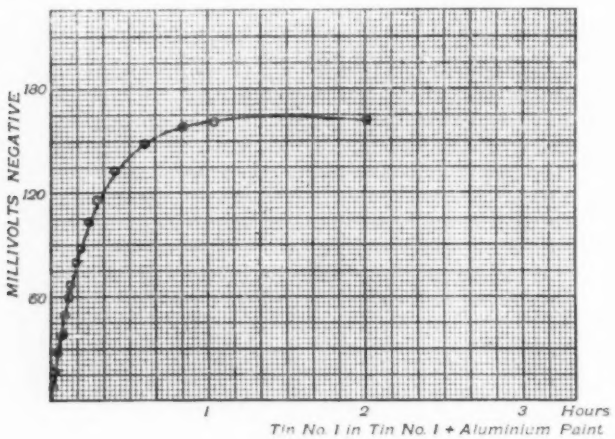

Fig. 5.

was observed on two different days, and would seem to indicate the presence of two opposing influences, one of which became insignificant as time went on.

(*b*) *Extent of the Charge and Variation in its Magnitude with Time.* —The charges in all the experiments were found to rise with vary-

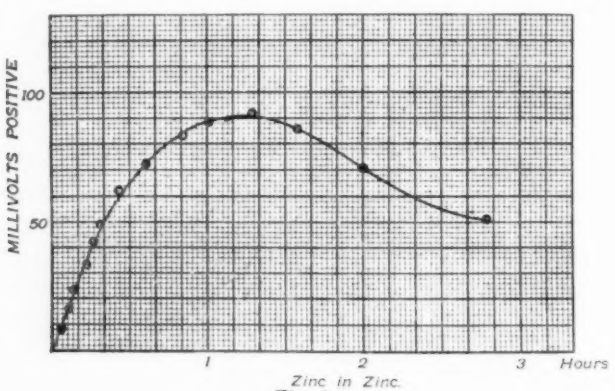

Fig. 6.

ing rates to their maximum values. These rates, however, were found to be very greatly increased by the presence of radium bromide. Typical sets of readings showing the rates at which the charge

was acquired with and without radium are given in Tables II. and III. Other sets of readings, illustrating various phases of the work are given in Tables, II., IV., V., VI., VII. and VIII., from which the curves shown in Figs. 3, 4, 5, 6, 7 and 8 are plotted.

TABLE IV.

*Tin No. 2 in Tin No. 2. Without Radium.*

| Time. | Deflection (in Millivolts). | Time. | Deflection (in Millivolts). |
|---|---|---|---|
| 1½ min. | 8 positive | 33 min. | 65 positive |
| 2⅔ " | 15 " | 44 " | 70 " |
| 4 " | 22 " | 78 " | 76 " |
| 5½ " | 28 " | 1 hr. 40 " | 80 " |
| 6¾ " | 33 " | 2 " 5 " | 80 " |
| 9¼ " | 42 " | 2 " 39 " | 82 " |
| 11⅝ " | 47 " | 2 " 51 " | 82 " |
| 19 " | 58 " | 4 " 1 " | 82 " |

Like McLennan and Burton, the writer found that the extent of the charge varied little with the size of the cylinders and with the sign of the charge on the needle of the electrometer. A double

TABLE V.

*Outer Cylinder—Tin No. 1 + Aluminium Paint. Inner Cylinder—Tin No. 1 + Aluminium Paint. Without Radium.*

| Time. | Deflection (Millivolts). | Time. | Deflection (Millivolts). |
|---|---|---|---|
| ¾ min. | 7 negative | 11½ min. | 88 negative |
| 1⅓ " | 12 " | 14½ " | 103 " |
| 1¾ " | 17 " | 17¾ " | 116 " |
| 3 " | 28 " | 24⅙ " | 133 " |
| 4 " | 38 " | 36 " | 149 " |
| 5½ " | 50 " | 50¾ " | 158 " |
| 6¾ " | 60 " | 1 hr. 3 " | 161 " |
| 7¾ " | 67 " | 2 " 1 " | 162 " |
| 10 " | 80 " | | |

combination was made by joining the two inner tin cylinders together by means of a piece of tin soldered to each, and also by joining in a similar way the two outer ones. With such an arrangement, the magnitude of the charge acquired (— 94 millivolts) was about the same as the maximum values for each combination

separately, namely, — 85 and — 91 millivolts (vide Table I., nos. 25, 26, 27; see also nos. 4, 14, 15, and compare Figs. 3 and 8).

The maximum value, it will be seen (vide Table I.), varied greatly with different combinations, and also was different at differ-

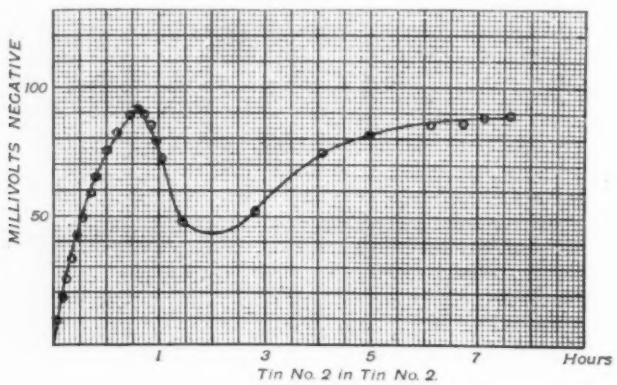


Fig. 7.

ent times of observation for the same combination. A good example of this latter effect is to be found in the case of lead no. 1 in lead no. 2 (vide Table I., nos. 4, 5, 6, 7, 8 and 9). Shortly after the cylinders had been cleaned the maximum negative charge acquired

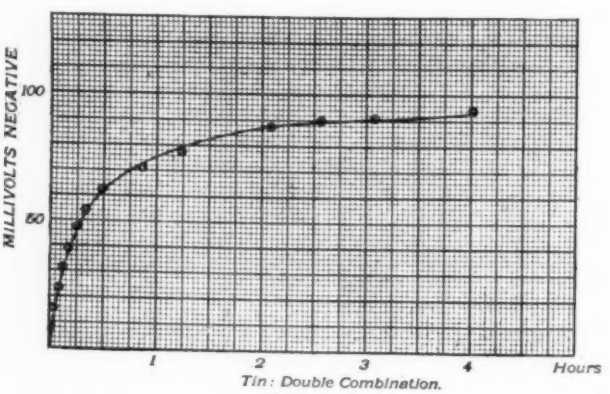


Fig. 8.

was 46 millivolts, one day later the value was 32, four days later 27, and twenty days later only 13. Another good illustration of this is the case of lead no. 1 in lead no. 3 (vide Table I., nos. 12 and 13), where the maximum value of the positive charge increased in fourteen days from 22 to 42 millivolts.

These results would seem to indicate the growth of a deposit or deposits removable by cleaning, which resulted in the insulated cylinders gaining a positive charge, and here we may have an explanation of the high positive charge which McKeon found for his lead

TABLE VI.

*Zinc in Zinc. Without Radium.*

| Time. | Deflection (Millivolts). | Time. | Deflection (Millivolts). |
|---|---|---|---|
| 3⅓ min. | 8 positive | 36½ min. | 72 positive |
| 6½ " | 16 " | 50⅝ " | 83 " |
| 8½ " | 23 " | 60½ " | 88 " |
| 11⅝ " | 33 " | 1 hr. 17½ " | 92 " |
| 16⅓ " | 42 " | 1 " 35 " | 86 " |
| 19 " | 49 " | 2 " | 71 " |
| 25½ " | 62 " | 2 " 47 " | 51 " |

combination. It is known that on old lead such as McKeon used, radioactive deposits are gradually formed, and on this account, there would be an emission of charged particles from both the inner and the outer cylinders. It is evident that this might result in a difference in the number of charged particles coming to the

TABLE VII.

*Tin No.* 2 *in Tin No.* 2. *Without Radium.*

| Time. | Deflection (Millivolts). | Time. | Deflection (Millivolts). |
|---|---|---|---|
| 3½ min. | 9 negative | 86½ min. | 89 negative |
| 10 " | 18 " | 1 hr. 33⅓ " | 85 " |
| 13⅔ " | 25 " | 1 " 38¼ " | 79 " |
| 18¾ " | 33 " | 1 " 43 " | 72 " |
| 23¾ " | 42 " | 2 " 3 " | 48 " |
| 27¾ " | 49 " | 3 " 11 " | 52 " |
| 35⅓ " | 59 " | 4 " 13 " | 75 " |
| 41¼ " | 65 " | 5 " | 81 " |
| 50½ " | 75 " | 5 " 57 " | 85 " |
| 61⅝ " | 82 " | 6 " 27 " | 86 " |
| 74¼ " | 89 " | 6 " 47 " | 88 " |
| 80⅓ " | 91 " | 7 " 12 " | 89 " |

insulated cylinder and in the number leaving it. It could then happen that the insulated cylinder would acquire a positive charge, the magnitude of which would be largely determined by the nature of the active deposits.

It was found, too, that the charge did not always remain at a maximum value. With some cylinders it gradually decreased in amount, and, in a few of these cases, a second rise was observed (vide Figs. 6 and 7). As noted above, with the combination lead no. 1 in lead no. 2, observations, for which the values are given in Table IX. and the curve representing them is shown in Fig. 1, were continued for an extended period of time. As, in this case, considerable variations were observed, it is possible that all the others

TABLE VIII.

*Tin No. 1 + Tin No. 2 in Tin No. 1 + Tin No. 2. Without Radium.*

| Time. | Deflection (Millivolts). | Time. | Deflection (Millivolts). |
|---|---|---|---|
| 57 sec. | 8 negative | 52⅔ min. | 71 negative |
| 2 min. 50 " | 15.5 " | 74½ " | 77 " |
| 5 " 5 " | 23 " | 2 hr. 5 " | 87 " |
| 7½ " | 31 " | 2 " 34 " | 90 " |
| 10⅔ " | 39 " | 3 " 5 " | 91 " |
| 15 " | 46.5 " | 4 " 1 " | 94 " |
| 20½ " | 54 " | 4 " 2½ " | 93 " |
| 29⅓ " | 62 " | | |

would have exhibited similar changes, had the observations been continued long enough. With these lead cylinders, which were freshly cleaned the day before readings were commenced, the highest maximum value of the negative charge acquired was about 64 millivolts (a scale deflection of about 33 mm.). At the end of the period of 67 hours, it was found that the zero had drifted 6.5 mm. to the negative side. The readings given in Table IX., however, were all corrected for this change in zero, and also for a gradual change in the sensibility of the electrometer due to a dropping in the potential of the storage cells used to charge the needle, from 170 volts to 144 volts.

In one or two cases where a drop from the initial maximum charge occurred, it was observed that, for the same combination, on different days the drop was not always in evidence (see Table I., compare nos. 28, 29 and nos. 32, 33). After the cylinders had been cleaned, tin no. 2 rose in about 4 hours to a maximum of 171 millivolts, and then dropped to 38. The next day, in the same

## TABLE IX.

*Lead No.* 1 *in Lead No.* 2.

| Time. | Deflection (Reduced to Millivolts). | Time. | Deflection (Reduced to Millivolts). |
|---|---|---|---|
| Wednesday 4.01 p. m. | 0 | Thursday 9.05 p. m. | 52.6 |
| " 4.02 " | 2 | " 10.00 " | 54 |
| " 4.03 " | 5 | " 11.05 " | 54.6 |
| " 4.05 " | 8 | " 12.00 " | 56 |
| " 4.08 " | 11 | Friday 1.05 a. m. | 57 |
| " 4.11 " | 13 | " 2.00 " | 59 |
| " 4.17 " | 16 | " 3.05 " | 60.5 |
| " 4.22 " | 18 | " 4.00 " | 62 |
| " 4.31 " | 21 | " 5.05 " | 63 |
| " 4.44 " | 25 | " 6.00 " | 63 |
| " 4.48 " | 27 | " 7.00 " | 63.5 |
| " 4.55 " | 29 | " 7.30 " | 63.3 |
| " 5.05 " | 32 | " 8.37 " | 64 |
| " 5.17 " | 33 | " 10.10 " | 64 |
| " 5.25 " | 34 | " 10.24 " | 61 |
| " 6.24 " | 40 | " 10.34 " | 60 |
| " 7.06 " | 42 | " 11.19 " | 63 |
| " 7.25 " | 43 | " 11.54 " | 56 |
| Thursday 12.30 a. m. | 36 | " 12.39 p. m. | 55 |
| " 1.00 " | 34 | " 12.54 " | 55.6 |
| " 1.40 " | 33 | " 1.55 " | 57.5 |
| " 1.52 " | 33 | " 2.25 " | 58 |
| " 2.55 " | 34 | " 2.52 " | 59.5 |
| " 3.55 " | 34 | " 3.30 " | 60 |
| " 4.55 " | 33 | " 4.26 " | 57.5 |
| " 6.00 " | 33.5 | " 4.43 " | 58 |
| " 7.00 " | 33 | " 6.18 " | 58 |
| " 8.00 " | 33 | " 7.05 " | 58 |
| " 8.48 " | 29 | " 8.00 " | 56 |
| " 9.37 " | 33 | " 9.05 " | 53 |
| " 10.08 " | 34.5 | " 10.00 " | 51 |
| " 10.40 " | 33 | " 11.00 " | 48.7 |
| " 10.52 " | 32 | " 11.30 " | 47.7 |
| " 11.20 " | 33.5 | " 12.00 a. m. | 47 |
| " 12.10 p. m. | 36 | Saturday 1.05 " | 47 |
| " 12.50 " | 39 | " 2.00 " | 41.7 |
| " 2.06 " | 42 | " 3.10 " | 37.9 |
| " 2.45 " | 46 | " 4.00 " | 37.8 |
| " 2.55 " | 47.5 | " 5.05 " | 35 |
| " 3.49 " | 50.5 | " 6.00 " | 34 |
| " 4.10 " | 55 | " 7.00 " | 32.8 |
| " 4.37 " | 53 | " 8.48 " | 31.2 |
| " 5.46 " | 50 | " 9.51 " | 31.4 |
| " 7.06 " | 50 | " 10.53 " | 30.1 |
| " 8.04 " | 52 | | |

time, it rose steadily to 82 millivolts. It is, of course, possible, that had the observations been continued long enough a drop might have been observed here too, and it should be mentioned that the former set of observations was taken between 3 p. m. and 7:30 p. m., while the latter were taken between 9:30 a. m. and 2 p. m. McKeon's explanation of these results as being due to daily variations in an external cause is possible, but it would seem that a more probable one is found in a change taking place in the surface of the metals, perhaps arising from modifications in the state of the atmospheric air.

(*c*) *Variation in the Magnitude of the Charge with the Intensity of Penetrating Rays.* — McKeon attributed the variations which he observed to changes in the amount of ionization of the enclosed air. That this cannot be the cause is shown by the fact that, while the presence of the radium affects very greatly the rate at which the charge is acquired, it modifies but little the maximum value. This was observed by McLennan and Burton, as well as by the writer.

McLennan and Burton also found that, when the cylinders were placed in a tank filled with water, the layer of water being 13 cm. thick, the maximum value of the charge was unchanged. By this means the natural radiation was lessened,[1] and yet the charge remained the same.

To further investigate the effect of varying the amount of ionization, some measurements were made on the charge acquired by the inner of two lead cylinders when some radium in a small glass tube was placed within the inner one and successively surrounded with a series of different thicknesses of sheet lead. In each case the charge acquired by the insulated cylinder rose in half a minute or less to a maximum value. From Table X. a comparison can be made of the values of the charge acquired in each case, and of the relative intensities of the radiation used to hasten the action. The intensities were compared by placing the radium with its different coverings at a fixed point near the electrometer, and measuring the current from the needle to the free quadrants.

It will be seen that while there were slight changes in the value

[1] Univ. of Toronto Studies, Phys. Science Series, No. 2; also PHYS. REV., Vol. XVI., No. 3, p. 184, 1903.

of the charge acquired, these were by no means proportional to the changes in the intensity of the radiation.

TABLE X.

| Remarks on Manner of Screening Radium. | Limiting Charge. Negative Arbitrary Scale. | Intensity of Radiation. Arbitrary Scale. |
|---|---|---|
| 1. In glass tube | 7.0 | 304 |
| 2. First covering of lead | 7.0 | 210 |
| 3. Second covering | 6.8 | 188 |
| 4. Third covering | | |
| 1st reading | 6.8 | 167 |
| 2d reading | 6.5 | 167 |
| 5. Fourth covering | | |
| 1st reading | 6.2 | 135 |
| 2d reading | 6.7 | 135 |

One must conclude, therefore, that, although variations do occur in the charge acquired by the inner insulated cylinder in combinations such as those investigated, these variations cannot be due to changes in the amount of ionization produced by the earth's penetrating rays. They may possibly be due, however, to some changes in the surface of the metals themselves, or to changes in the radiations given off by these metals.

It is possible that further light may be thrown on these experiments by measurements similar to a series which the writer has recently made in seeking to determine the contact potential difference between two metals, by using a modification of the apparatus used in the early part of this investigation.

## IV. VOLTA EFFECT.

In these experiments the following apparatus (Fig. 9) was used:

A circular copper plate $AB$ about 9 cm. in diameter was joined to the electrometer by means of a conductor of the same material, insulated from a surrounding earthed tube by means of amber. A box $CC'$, $DD'$, also of copper, served as a guard ring to the plate $AB$, and as a screen from electrostatic disturbances. Above the plate $AB$ and insulated from it by small amber supports, a second plate $HK$ of a selected metal was placed, and this was kept joined to earth while experiments with it were being made. Over all a wooden box $MM'$, $NN'$, lined with tin foil, was placed to complete the electric screening.

With both the plates $AB$ and $HK$ joined to earth, on account of the contact potential difference between them, there would be a current set up between them, if any free ions existed in the intervening space. If, with this arrangement, the earth connection to the lower plate were broken, this plate would, as a result of the current, acquire a charge which would tend to annul the original contact

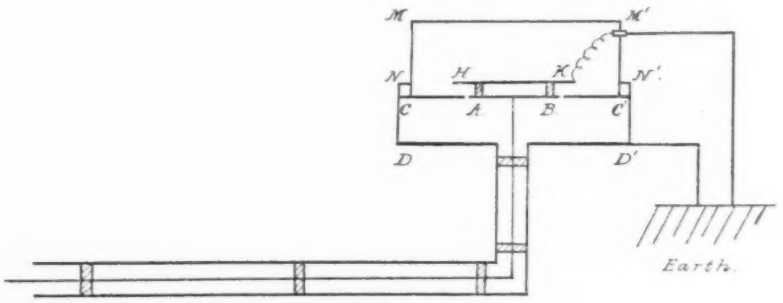


Fig. 9.

difference. It was therefore thought that, by placing a strong ionizing agent, such as radium, above the plates, the needle would, on breaking the earth connection to the lower plate, at once take up a maximum deflection, and so give a measure of the contact difference.

It was found that, by using strong radium near the plates, the lower one did acquire in a very few minutes a maximum charge. It was found, too, that as the radium was removed farther and farther from the apparatus, the rate at which this maximum was reached became slower and slower.

It has been found, however, as a result of the experiments so far performed, that the value of this maximum charge varied, (1) with the material and the thickness of the upper plate, (2) with the distance between the plates, (3) with the distance of the radium from the plates.

TABLE XI.

| Upper Plates (Lower Plate Copper). | Sign and Magnitude of Charge Acquired by Free Copper Plate. | |
|---|---|---|
| | 2 mm. Apart, Millivolts. | 10 mm. Apart, Millivolts. |
| Aluminium | − 9 | +289 |
| Zinc (thin) | + 4 | +277 |
| Zinc (thick) | −15 | +261 |
| Lead | +38 | +212 |
| Copper (thin) | −68 | − 79 |
| Copper (thick) | −85 | − 48 |

Table XI. gives the results of some measurements made by using different upper plates. The metals are arranged in the order in

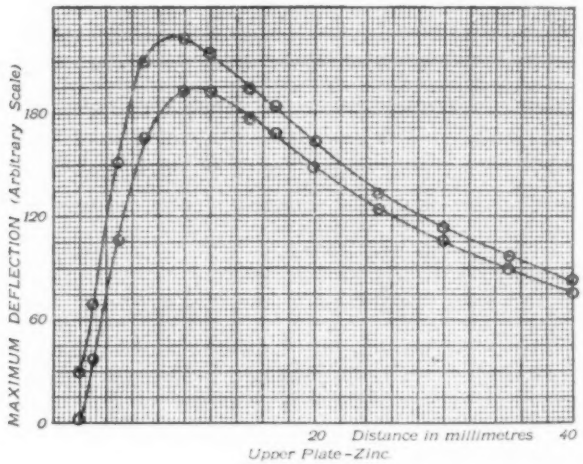


Fig. 10.

which they occur in the Volta series, and it will be seen from the values of the maximum potentials recorded that other influences besides the Volta effect must have contributed to the result. The

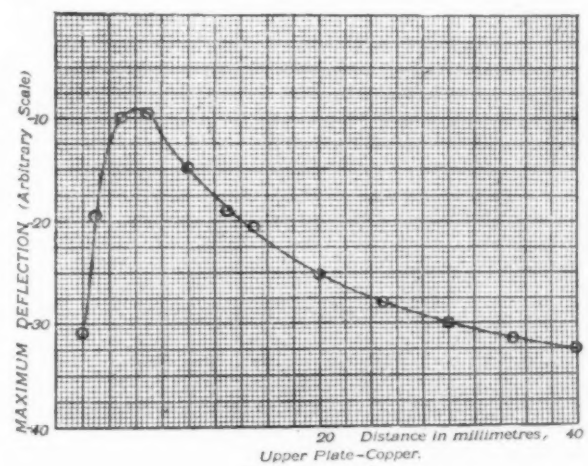


Fig. 11.

values obtained are very much lower than the contact potential differences usually recorded. Further, although aluminium and

zinc come higher in the contact series than lead, yet, when the plates were 2 mm. apart, lead gave a higher positive potential to the copper plate than either of them. Indeed, aluminium and the thicker zinc plate, as will be seen, gave a slightly negative value to it. With both the zinc and copper plates, an increase in the thickness resulted in an increased negative charge on the free copper plate.

It will be observed, also, that when the plates were 10 mm. apart, there was a marked positive increase in the values. This was more carefully investigated by taking a series of measurements with different distances between the plates. The results obtained are given in Tables XII. and XIII., and are illustrated by the curves in Figs. 10 and 11. It will be seen that, as the distance between the plates was increased, the values of the charge acquired became more and more positive, until a maximum point was reached, after which the values became more negative.

TABLE XII.

*Upper Plate. Zinc.*

| Distance Between Plates. | Deflection for Thin Plate. | Deflection for Thick Plate. 1 Volt = 550 mm. |
|---|---|---|
| 2 mm. | + 30 mm. | + 2 mm. |
| 3 " | 69 " | 37 " |
| 5 " | 151 " | 106 " |
| 7 " | 209.5 " | 165.5 " |
| 10 " | 223 " | 193 " |
| 12 " | 214.5 " | 192.5 " |
| 15 " | 194 " | 176 " |
| 17 " | 183.5 " | 168 " |
| 20 " | 163.5 " | 148 " |
| 25 " | 132.5 " | 123.5 " |
| 30 " | 114 " | 105.5 " |
| 35 " | 97 " | 91 " |
| 40 " | 83 " | 77 " |

In these latter experiments it must be remembered that not only was the distance between the plates varied, but, since the radium was kept in a fixed position, the distance from the upper plate to the radium, as a consequence, was varied also. That this is an important factor is shown by the results of some measurements made with the radium at various distances from the plates, which were kept at fixed distances apart.

The results obtained are given in Tables XIV., XV. and XVI., and are represented graphically by the curves in Figs. 12, 13 and 14. From these it will be observed that as the distance of the radium was increased, there was a gradual decrease in positive values or an increase in negative ones until a minimum point was reached. After this there followed a slight increase in the positive or a decrease in the negative readings. The appearance of a final maximum is suggested, but not well marked by the form of each of the curves.

TABLE XIII.

*Upper Plate. Copper.*

| Distance Between Plates. | Deflection. 1 Volt = 550 mm. | Distance Between Plates. | Deflection. 1 Volt = 550 mm. |
|---|---|---|---|
| 2 mm. | — 31 mm. | 15 mm. | — 20.5 mm. |
| 3 " | — 19.5 " | 20 " | — 25.2 " |
| 5 " | — 10 " | 25 " | — 28 " |
| 7 " | — 10.4 " | 30 " | — 30 " |
| 10 " | — 15 " | 35 " | — 31.5 " |
| 13 " | — 19 " | 40 " | — 32.5 " |

In order to ascertain exactly whether the potential acquired by the free plate continued to approximate to a final steady value, a set

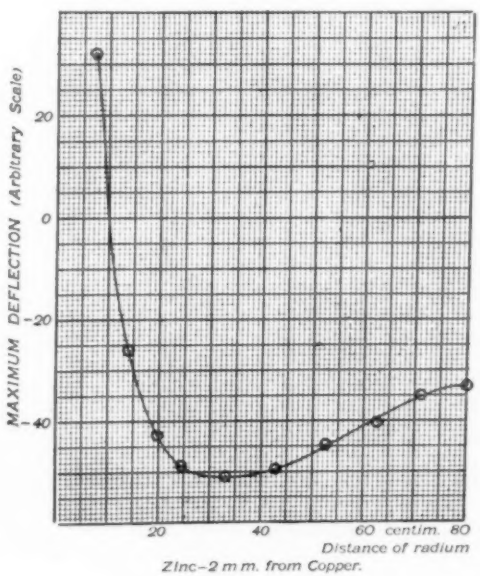


Fig. 12.

of observations was taken with the two copper plates at 2 mm. apart, when the radium was moved through a more extensive range

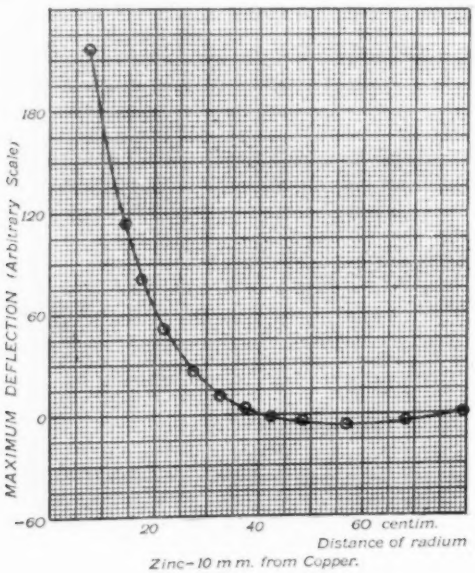


Fig. 13.

of distances. These results, which are recorded in Table XVII., and are represented by the curve given in Fig. 15, show that the charge on the free plate did not continue to approach a steady value,

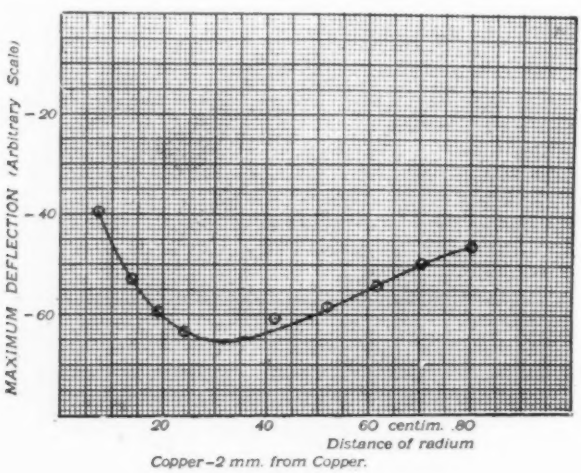


Fig. 14.

but that as the radium was removed very considerable variations occurred in the magnitude of the charge. Some readings were also taken of the potential acquired by the free copper plate without the use of radium, when both zinc and copper plates were placed at

TABLE XIV.

*Upper Plate. Zinc. Distance Between Plates — 2 mm.*

| Distance of Radium. | Deflection. 1 Volt = 575 mm. | Distance of Radium. | Deflection. 1 Volt = 575 mm. |
|---|---|---|---|
| 7.3 cm. | + 32 mm. | 42.9 cm. | − 49.5 mm. |
| 14.1 " | − 26 " | 52.8 " | − 44.8 " |
| 19.8 " | − 42.8 " | 62.8 " | − 40.4 " |
| 24.6 " | − 48.8 " | 71.2 " | − 35 " |
| 32.1 " | − 50.8 " | 80.2 " | − 33 " |

different distances above it. These results are recorded in the first column of Table XVIII. For the purpose of comparison the final maximum values obtained in the cases illustrated by the curves 12, 13 and 14 are also recorded in the second column of this table. From these results it will be seen that in every case the

TABLE XV.

*Upper Plate. Zinc. Distance Between Plates — 10 mm.*

| Distance of Radium. | Deflection. 1 Volt = 522 mm. | Distance of Radium. | Deflection. 1 Volt = 522 mm. |
|---|---|---|---|
| 7.3 cm. | + 215.5 mm. | 37.4 cm. | + 4.5 mm. |
| 14.4 " | + 114.5 " | 42.2 " | − 1 " |
| 21.9 " | + 51.5 " | 48.6 " | − 4 " |
| 17.6 " | + 81 " | 56.8 " | − 6 " |
| 27.5 " | + 26.5 " | 68.1 " | − 4.5 " |
| 32.6 " | + 11.5 " | 79.6 " | + 0.5 " |

values obtained without the radium were more positive than those obtained with it.

One would have expected that as the radium was removed the values given in Column II. of Table XVIII. would have approximated to those obtained without the radium and recorded in Column I., but their failure to do so can probably be traced to the difficulty experienced in obtaining satisfactory readings when the radium was placed at the longer distances or entirely removed. Under these

circumstances the rate of deflection was exceedingly slow and consequently the readings, owing to the comparatively small capacity of the plate system, were subject to large errors arising from disturbances to the measuring system which with the radium nearer were negligible.

TABLE XVI.

*Upper Plate. Copper. Distance Between Plates — 2 mm.*

| Distance of Radium. | Deflection. 1 Volt = 540 mm. | Distance of Radium. | Deflection. 1 Volt = 540 mm. |
|---|---|---|---|
| 7.3 cm. | − 39.5 mm. | 41.8 cm. | − 60.8 mm. |
| 13.8 " | − 53 " | 52.0 " | − 58.5 " |
| 19.2 " | − 59.5 " | 61.8 " | − 54.5 " |
| 24.2 " | − 63.5 " | 70.4 " | − 49.8 " |
| 31.9 " | − 65.5 " | 80.4 " | − 46.5 " |

In analyzing the observations made on the Volta effect in the plate experiments it is difficult to account for all the results. It is evident that at least two influences were present, namely, (1) the conductivity of the air between the plates and (2) secondary radiation, and it is clear that each contributed with the different combinations to the magnitude and sign of the charge acquired.

TABLE XVII.

*Upper Plate. Copper. Distance Between Plates — 2 mm.*

| Distance of Radium. | Deflection. 1 Volt = 570 mm. | Distance of Radium. | Deflection. 1 Volt = 570 mm. |
|---|---|---|---|
| 7.3 cm. | − 47.8 mm. | 59.0 cm. | − 54 mm. |
| 10.5 " | − 47.5 " | 80.1 " | − 55 " |
| 16.0 " | − 50.5 " | 108.0 " | − 56.2 " |
| 24.7 " | − 55 " | 156.3 " | − 51.5 " |
| 31.2 " | − 57.5 " | 204 " | − 54.4 " |
| 41.7 " | − 56.5 " | | |

That conductivity is an important factor in determining the limiting charge given to the free plate was shown by simply blowing filtered air between the plates. It was found that in all cases, where the upper plate was positive to the lower, positive values were decreased by blowing. On the other hand, by using a carbon plate above, so as to make the copper plate below acquire a negative charge through the Volta effect, the negative deflection was also lessened by the same means.

TABLE XVIII.

| Plates. | Column I., Without Radium. | Column II., With Radium at Greatest Distance. (In Figs. 12, 13, 14, 15.) |
|---|---|---|
| Zinc, 2 mm. from copper | +37 millivolts. | −57 millivolts. |
| Zinc, 10 mm. from copper | +27 " | + 1 " |
| Copper, 2 mm. from copper | −33 " | −90 " |

It has been shown by Professor MacKenzie[1] that the secondary radiation from the back of metallic plates, upon which the rays from radium are allowed to fall, is of considerable importance. Negative particles, will, under these circumstances, come to the lower plate from the upper, while there will also be an emission of negative particles from the lower one itself. The nature of the charge acquired by the lower plate will be determined, therefore, in a measure by

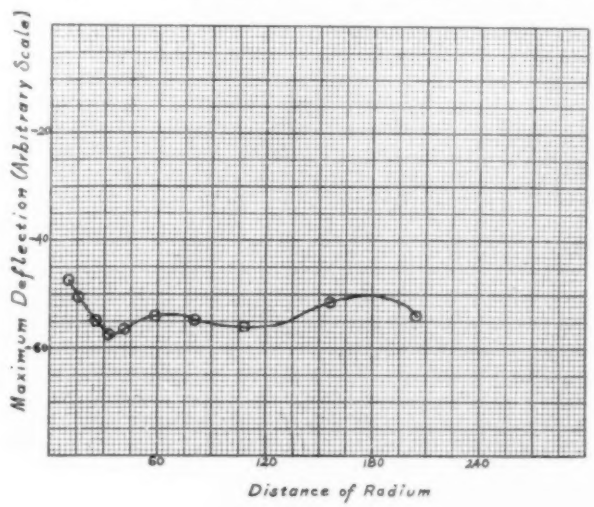


Fig. 15.

the ratio of the number of particles leaving it to the number coming to it. An alteration in this ratio would take place when both the thickness and the material of the plates were varied, when the distance between the plates was altered, and when the distance of the radium was increased, and it is quite conceivable therefore that this ratio could vary in such a manner as to give rise to the results obtained.

From the experiments which have been cited in this paper, it is

[1] Phil. Mag., July, 1907.

evident that the manner in which insulated metallic cylinders surrounded by others joined to earth, or insulated plates of metal placed close to others of the same or of different metals become electrically charged is both complex and obscure. It is clear, too, that both the Volta effect and secondary radiation are influences affecting the process of charging, and although the experiments of the present investigation throw considerable light on the relative influence of these two factors, it will be necessary to take more extensive observations before a complete explanation can be offered.

In conclusion the writer wishes to express his sincere thanks to Professor McLennan for his kindly interest and helpful suggestions during the progress of the investigation.

PHYSICAL LABORATORY,
UNIVERSITY OF TORONTO, May 25, 1908.

# AN INVESTIGATION OF THE ELECTRIC INTENSITIES AND ELECTRIC DISPLACEMENT PRODUCED IN INSULATORS BY THEIR MOTION IN A MAGNETIC FIELD.[1]

By S. J. Barnett.

## Introduction.

FROM the classical experiments of Ampère and Rowland it follows that an electrified particle with charge $q$ moving with velocity $v$ in a magnetic field at a point where the induction is $B$ is acted upon by a force $F$ equal, if suitable units are used, to the product of the charge $q$ by the vector product of the velocity $v$ and the induction $B$. That is,

$$F = qVvB. \tag{1}$$

Hence if ether or matter is electrically constituted and moves in a magnetic field, each moving electrified constituent is acted upon by an electromagnetic force in accordance with (1); that is, the moving substance is the seat of an intrinsic electric intensity $f$, the "motional intensity" of Mr. Heaviside, given by the equation

$$f = F/q = VvB. \tag{2}$$

The relative displacement of the oppositely electrified constituents of the moving substances produced by the motional intensity $f$ gives rise to an electric field; and the intensity $E$ of this field acts on all dielectrics which the field contains, whether at rest or in motion. If both ether and matter move, both intensities act on both substances. But if the ether remains fixed and the matter moves through it, the intensity $f$ acts on the matter only, while the field intensity $E$ acts on both the ether and the matter. The actual electric displacement, if the matter is insulating, depends only on

[1] Presented in part to the American Physical Society, October 19, 1907.

The paper describes also some observations on an electrical effect produced in certain cases by rotation in a region not a magnetic field.

both intensities and on the dielectric constants of the matter and the ether. If the medium is conducting, much simplification arises when the current density is zero. If the current density is not zero, other considerations must be introduced.

The existence of the motional intensity in conductors was discovered by Faraday in 1831, and the subject has been studied in detail by him and many others. The results of all experiments which have been made upon the subject are in accord with the theory given in equation (2).

The first experiments on the motional intensity and displacement in insulators were published by Blondlot[1] early in 1902. In these experiments a stream of dust-free air was passed with a variable velocity between the rectangular pole-faces *NS* of a magnet and two rectangular brass plates *AB* and *CD* arranged as shown in Figs. 1

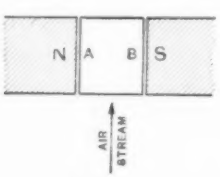


Fig. 1.

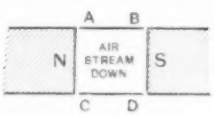


Fig. 2.

and 2. The velocity of the air was parallel to the pole-faces and the plates, and perpendicular to the lines of magnetic intensity stretching through the central part of the field. When the velocity of the air was a maximum the plates *AB* and *CD* were connected together metallically for an instant. Then one of the plates was removed and tested for charge. The charge to be expected on the hypothesis that the ether moves with the matter was many times greater than the smallest charge that could be detected; while the charge to be expected on the hypothesis that the ether remains fixed while the matter moves through it was far less than the smallest charge that could be detected. In the experiments no charge was detected. Thus the investigation confirmed the theory of Lorentz, according to which the ether is fixed.

The only other investigation hitherto published on the subject is

[1] Journal de Physique, January, 1902.

that of H. A. Wilson,[1] who made experiments on ebonite in 1903 and 1904. These experiments also, which will be further discussed below, support the theory of Lorentz.

The investigation described here was begun, in a way, in 1902, when a piece of apparatus was designed and partially constructed. Lack of funds, however, put an early end to the work. Its continuance was made possible by a grant received from the Carnegie Institution early in 1904. The design of apparatus submitted to the institution was then gone over carefully and very greatly improved, though no experimental work was practicable until near the summer of 1906. In the meantime, experience in another investigation, not yet completed, together with some serious troubles which Dr. Wilson's method of experiment gave him, convinced me of the very great difficulties involved in low voltage electrostatic work when insulated slipping contacts are used, and when insulators or insulated conductors move in air not free from dust. To eliminate these difficulties and to secure other important advantages, the apparatus used in the investigation as finally carried out was constructed on lines quite different from those proposed to the Carnegie Institution. In some important respects it resembles the apparatus used by Wilson, while in many others it differs greatly therefrom.

## Method and Theory.

A diagram of the principal pieces of apparatus used in the electrostatic part of the experiment proper is given in Fig. 3. In order to save space later the description given here is more complete than would otherwise be advisable. The insulator under investigation has the form of a hollow circular cylinder $A$ fitted closely on a coaxial rotor $B$ of bronze. This rotor revolves centrally and symmetrically within a large cylindrical coil $C$ of copper wire wound on a brass bobbin $D$. The magnetic field is produced by a current in this coil. The bearings $EE$ in which the rotor $B$ moves are screwed to the flanges forming the ends of the bobbin $D$. The cylinder $A$ is covered with a thin conducting coat $F$. A little longer than $A$, and surrounding it coaxially, is a uniform brass tube $G$. Surrounding this are the coaxial brass tubes $H$ and $D$, the latter a part of the

[1] Roy. Soc. Phil. Trans., Series A, September, 1904.

bobbin, and both together forming, with the brass rings soldered between them near the ends, a jacket for water or air. The tube $G$ is insulated from $H$ by small blocks of amber. Between these two tubes is a brass rod $JJ$ capable of being rotated in the brass bearings

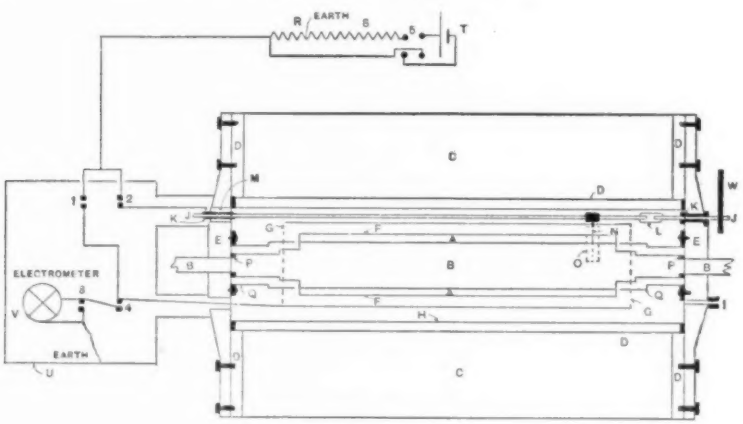


Fig. 3.

$KK$ near its ends. The rod is cut near its S. end and the two parts are separated by a block of amber $L$. At the N. end the bearing $K$ is surrounded by an amber block $M$, which insulates it from the bobbin. Screwed to the insulated, or N., part of the rod $JJ$ is a stiff curved brass wire $N$ by which this part of the rod may be brought into contact with the metal coat of $A$ without touching the tube $G$. For this purpose a small slit $O$ is cut in $G$. Small ebonite rings $PP$ make the electrical contacts between the rotor $B$ and the bearings always nearly the same. Brass tubes $QQ$, of very nearly the same diameter near the rotor as that of the part of the rotor within $A$, and coaxial with $A$, extend from the bearings $EE$ almost into contact with $B$, and form electric screens. A potentiometer $RS$ and battery $T$, with commutator 5, produces the voltage (along $R$) used for standardization purposes. An electrometer $V$ is the principal measuring instrument. Potentiometer and electrometer connections with $J$ and $G$ are made by amber keys 1, 2, 3, 4, of special design described below. Except as shown in the figures, the space holding the electrometer and its connections is practically metal enclosed. The metal case is earthed.

When the coil $C$ is traversed by an electric current, the region occupied by the bronze rotor, the insulating cylinder, and its metal coat, becomes a magnetic field, in the central part of which the lines of intensity are parallel to the axis of the rotor. In the rest of this region there is a component of the intensity in this direction. Hence, by (2), when the rotor is revolved, a motional electric intensity is developed in the moving bodies, radial in the central portions and with a radial component elsewhere. If the motional intensity is directed outward, the intensity of the resulting electric field will be directed inward in the moving insulator and conductors, and it will be directed outward in the air between the tubes $F$ and $G$, which is supposed to be earthed, since the voltage from any point $P$ of $F$ to $G$ is the same as that from $P$ to the earthed bearings through $F$, the insulator, and the bronze rotor. We proceed to the calculation of the mean potential of the outer surface of $F$. When the value of this quantity on any theory has been determined, an experimental method can be devised for testing the validity of this theory.

### Potential of $F$, Ideal Case.

Consider first, for simplicity, the ideal case in which the magnetic field is uniform throughout the entire length of the moving parts; the insulator $A$ so long that sensibly all the lines of intensity in the electric fields are radial, the end effects being entirely neglible; the rotor, an infinitely thin tube, of the same diameter throughout, and its surface everywhere at zero potential, and the thickness of the conducting tube $F$ neglible. The number of revolutions made by the rotor per second will be denoted by $n$.

The ether will at first be assumed to remain fixed. The motional intensity within the insulator at a distance $r$ from the axis is

$$f = V_0 B = 2\pi r n B$$

in magnitude, and will be considered positive when directed outward. If the electric field intensity at the same distance from the axis in the resulting field is denoted by $E$, considered positive when directed outward, the total electric intensity acting on the matter, not including the ether, is $f + E$, and the electric displacement in the matter alone is

$$D = (K - 1)(f + E),$$

$K$ being the dielectric constant of the matter including the ether, and 1 being the dielectric constant of the ether.

The outward electric flux in the insulator, due to this displacement, across a cylinder of radius $r$ coaxial with $A$ and of the same length $l$, is

$$D \cdot 2\pi rl = (K-1)(f+E)2\pi rl;$$

and this is equal to the electric flux back through the ether within $A$ together with that from the outer surface of $A$ to the earthed conductors, the total charge upon $F$, which is insulated, being zero.

Let the capacity which the condenser $ABF$ would have if its dielectric were ether only and its field wholly confined to the region occupied by the dielectric $A$ be denoted by $S$; the capacity of the part of the field whose tubes of displacement stretch between $F$ (and its connections, if any) and $G$ (which is earthed), by $S'$; and the voltage from the cylinder $F$ to the rotor $B$, or the potential of $F$, by $V$. Then we have, from the last paragraph,

$$(K-1)(f+E)2\pi rl = 4\pi(SV + S'V) = 4\pi(S+S')V,$$

and therefore also

$$f = \frac{2(S+S')V}{(K-1)lr} - E.$$

The motional E.M.F. $\Psi$ from $B$ to $F$ through the cylinder $A$, with internal and external radii $r_1$ and $r_2$, is thus

$$\begin{aligned}\Psi &= \int_{r_1}^{r_2} f\,dr = \frac{2(S+S')V}{(K-1)l}\int_{r_1}^{r_2}\frac{dr}{r} - \int_{r_1}^{r_2} E\,dr \\ &= V\left[\frac{S+S'}{K-1}\cdot\frac{1}{\dfrac{l}{2\log r_2/r_1}} + 1\right] = V\left[\frac{S+S'}{(K-1)S} + 1\right].\end{aligned} \tag{3}$$

We have also

$$\Psi = \int_{r_1}^{r_2} f\,dr = 2\pi nB\int_{r_1}^{r_2} r\,dr = nB(\pi r_2^2 - \pi r_1^2), \tag{4}$$

*i. e.*, the rate at which magnetic flux is cut by any line fixed in the dielectric and extending from $B$ to $F$. The sign of $\Psi$ is the same as that of $f$ or $VvB$.

Equation (3) may be written

$$V = \Psi \frac{(K-1)S}{KS+S'}. \tag{5}$$

And, if $S''$ is written for $KS$, the actual capacity of the condenser $ABF$ when its field is confined entirely to the dielectric $A$, this becomes

$$V = \Psi \frac{(K-1)S''}{K(S''+S')}. \tag{6}$$

If the ether is not at rest, but moves with the same velocity as that of the matter it permeates, we must write $K$ in place of $K-1$, and remove $S$, in (3) and the preceding equations. We thus obtain, on this hypothesis,

$$V = \Psi \frac{S''}{S''+S'}. \tag{7}$$

Also, if $A$ were a conductor, instead of an insulator, we should have $K = \infty$, and therefore

$$V = \Psi \frac{S''}{S''+S'} \tag{8}$$

as in (7). Thus the same expression is obtained in the case of a conductor whether the ether is at rest or in motion.

THE ELECTRIC FIELD WITHIN THE INSULATING CYLINDER.

This field will be discussed here for two interesting cases only, viz., (1) that in which the metal tube $F$ either does not exist or is disconnected from all other conductors, and (2) that in which the tube $F$ is connected with the rotor $B$ by a wire at rest, so that the voltage between $F$ and $B$ is zero. In both cases $f$ and $E$ will be considered positive when directed radially outward.

In case 1, the *total* displacement $D$ at all points of a cylinder of radius $r > r_1 < r_2$, coaxial with $A$, is, if the ether is at rest,

$$D = (K-1)f + KE = KE + (K-1)\omega rB = 0,$$

where $\omega = 2\pi n$; so that

$$E = -\frac{K-1}{K} f = -\frac{K-1}{K} \omega Br. \tag{9}$$

Within the hollow rotor and outside the tube $F$ or the external surface of the dielectric $A$, there is no intensity.

When $F$ and $B$ are connected by a conductor, as in case 2, all the lines of field intensity traversing the *whole* distance between $B$ and $F$ disappear, the voltage being reduced to zero. But the field intensity does not vanish except over one cylinder of radius $r_0$ to be determined. If it did, the charge on the tube $F$ would be greater than the opposite charge on the rotor $B$, and the dielectric itself would be internally charged, since $f$ increases proportionally with $r$, and $D$ would therefore increase in the same way. The voltage through $A$ being zero, the direction of the field intensity, always radial, changes in sign at the cylinder of radius $r_0$. Within this cylinder $E$ has the same direction as $f$, so as to increase the total displacement; while outside this cylinder it has the opposite direction, so as to decrease the displacement which would exist were $f$ alone acting. Over the cylinder of radius $r_0$ the field intensity vanishes. In this way the voltage between $B$ and $F$ is kept zero, and the electric flux across all cylinders which can be drawn between $B$ and $F$ is kept constant and equal to that across the cylinder of radius $r_0$. $E$, $r_0$, and $q$, the charge per unit length upon $B$, can be determined as follows:

The outward electric flux across unit length of a cylinder of radius $r$ is

$$4\pi q = [(K-1)f + KE]2\pi r = [(K-1)\omega Br + KE]2\pi r.$$

If we put $r = r_0$, and therefore $E = 0$, this equation becomes

$$4\pi q = (K-1)\omega B \cdot 2\pi r_0^2. \tag{10}$$

From these equations

$$E = \frac{K-1}{K}\frac{\omega B}{r}(r_0^2 - r^2). \tag{11}$$

The radius $r_0$ can be obtained from (11) and the consideration that the voltage between $B$ and $F$ is zero. Thus

$$0 = \int_{r_1}^{r_2} E dr = \frac{K-1}{K}\omega B \int_{r_1}^{r_2}\left(\frac{r_0^2}{r} - r\right) dr,$$

or

$$r_0^2 \log\frac{r_2}{r_1} - \tfrac{1}{2}(r_2^2 - r_1^2) = 0;$$

whence

$$r_0 = \left(\frac{r_2^2 - r_1^2}{2 \log r_2/r_1}\right)^{\frac{1}{2}} \qquad (12)$$

If the ether moves with the matter, $K - 1$ must be replaced by $K$

MEAN POTENTIAL OF $F$, ACTUAL CASE.

In the actual case the magnetic field is not uniform throughout the rotating parts of the apparatus, the cylinder $F$ is not of neglible thickness, the cylinders may not be so long that the end effects can be entirely neglected, and their diameters are not perfectly uniform. The rotor $B$ is solid, moreover, or may be made of a thick tube, and its surface potential is not uniform and may be nowhere zero.

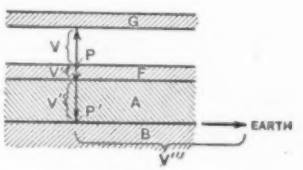


Fig. 4.

Consider any point $P$, Fig. 4, on the outer surface of the cylinder $F$. Let the potential of $P$ be denoted by $v$, the voltage through $F$ radially inward by $v'$, the voltage along the same radius through $A$ by $v''$, and the potential at $P'$, the point of the rotor's surface on the same radius, by $v'''$. Then

$$v = v' + v'' + v''',$$

and the average value $V$ of $v$ over the surface of $F$ is equal to the sum of the average values $V'$, $V''$, and $V'''$ of $v'$, $v''$, and $v'''$. That is

$$V = V' + V'' + V'''.$$

Let $f$ denote the outward radial component of the motional intensity at any point of $A$ or $F$ distant $r$ from the axis, $e$ the outward radial component of the intensity of the electric field at the same point, $S$ the capacity the portion of the field whose tubes stretch between $B$ and $F$ would have if its dielectric were ether alone, and $S'$ the capacity of the part of the field whose tubes stretch between $F$ and the conductors at zero potential, chiefly the tube $G$ and the screens $QQ$. Also let $F$ and $E$ denote the average values of $f$ and $e$ over the cylinder of radius $r$, whose length, $l$, is equal to that of $A$ and $F$. Then, on the theory of Lorentz,

$$(K-1)(F+E)2\pi rl = 4\pi(SV'' + S'V).^{1}$$

For the total charge upon $F$ is zero; and therefore the flux *to* $F$ due to the electric displacement of the moving, or material, portion of the insulator $A$ is equal to the flux *from* $F$ in the ether and air.

Thus the average value $\Psi$ of the motional E.M.F. $\psi$ from $B$ to $F$ is

$$\Psi = \int_{r_1}^{r_2} F dr = \frac{2(SV'' + S'V)}{(K-1)l} \int_{r_1}^{r_2} \frac{dr}{r} - \int_{r_1}^{r_2} E dr. \qquad (13)$$

The extreme radii $r_1$ and $r_2$ are mean values; but the cylinders can be turned so true that their departures from uniformity in diameter can be neglected. If we write

$$S''' = \frac{l}{2 \log r_2/r_1}, \qquad (14)$$

*i. e.*, the capacity $FAB$ would have if its dielectric were ether alone, and its field an entirely straight-line field between $B$ and $F$, and if we denote the average voltage in the conductors, viz., $V' + V''''$, by $U$, (13) may be written

$$\Psi = V - U + \frac{S(V-U) + S'V}{(K-1)S'''}, \qquad (15)$$

or

$$V = \frac{(K-1)S'''(\Psi + U) + SU}{(K-1)S''' + S + S'}. \qquad (16)$$

If $S''$ denotes the actual capacity of the condenser $FAB$, so far as this depends on the tubes of displacement stretching between $F$ and $B$, then

$$(K-1)S''' + S = KS''' + (S - S''') = S'' \qquad (17)$$

very approximately. Also, in the apparatus used in this investigation,

$$S - S''' = 0 \qquad (18)$$

with neglible error, on account of the smallness of the ratio of the thickness to the length of the cylindrical condenser and the presence of the screens $QQ$. Hence the expression for $V$ may be written

$$V = \left(\frac{K-1}{K}\Psi + U\right)\frac{S''}{S'' + S'}. \qquad (19)$$

[1] Inasmuch as the voltages $V'$ and $V''$ are not uniform the capacities involved differ slightly from $S$ and $S'$. The differences are here neglected.

## Formulation of Equation for Experimental Test. Calibration.

The quantity $V$ cannot be measured directly without an insulated sliding contact, which, unless in the form described near the end of this paper, introduces very great difficulties and should be avoided. Hence we proceed as follows:

The charge upon the outer coat of $F$, at the average potential $V$, is $S'V$; and a charge very approximately $-S'V$ exists on the inner surface and ends of the cylinder $G$. Some of the tubes from $F$ end on the screens $QQ$, however, and some on the other earthed conductors, so that the charge on $G$ is not exactly $-S'V$. If now $G$ is insulated and then connected with the electrometer, and if $F$ is earthed, an electrometer deflection $d$ will be produced such that

$$Cd = -S'V = -\left(\frac{K-1}{K}\Psi + U\right)\frac{S''S'}{S''+S'}, \qquad (20)$$

where $C$ is a constant.

To use this equation and to simplify the experimental work we must proceed further as follows: First the metal cylinders $F$ and $G$ are connected together by the rod $J$, the wire $N$, and the keys, and charged to a common potential $V_0$, while $B$, with the other conductors, remains earthed. Owing to the presence of $G$, which now acts as a guard cylinder, the charge $q_0$ taken by $F$ is confined to its inner surface except close to the ends, and the electric field near the ends of $A$ is more nearly like that at the center than it would be if the tube $G$ were absent. The actual capacity of the condenser $FAB$ with this field is very approximately the capacity already denoted by $S''$, and but few tubes of displacement stretch between the ends of $F$ and the screens $QQ$, owing to the field of the guard-tube $G$. Hence, very approximately,

$$q_0 = S''V_0.$$

After the cylinders have become charged, $N$ is raised, thus insulating $F$ from $G$ and $J$, and then both $G$ and $J$ are earthed. The inner surface of $G$ has now received a charge $q'$ given very approximately by the equation

$$q' = -q_0\frac{S'}{S''+S'}.$$

The cylinder $G$ is now insulated and connected to the electrometer, and $F$ is earthed. The charge $q'$ is distributed over the insulated system, and the electrometer gives a deflection $d_0$ proportional thereto by the constant $C$ of equation (20). Thus

$$q' = Cd_0 = -q_0 \frac{S'}{S'' + S'} = -V_0 \frac{S''S'}{S'' + S'}. \tag{21}$$

Dividing the equation (20) for $Cd$ by the equation (21) for $Cd_0$, and multiplying by $V_0$, we obtain

$$\frac{d}{d_0} V_0 = \frac{K-1}{K} \Psi + U. \tag{22}$$

Let $I$ denote the current in the coil, $\tau$ the time of one revolution of the rotor, and $\overline{\Psi}$ and $\overline{U}$ the values of $\Psi$ and $U$ when $I$ and $\tau$ are unity. Then

$$\Psi = \overline{\Psi} \frac{I}{\tau} \quad \text{and} \quad U = \overline{U} \frac{I}{\tau}.$$

Thus equation (22) may be written

$$V_0 \frac{d}{d_0} = \left[ \overline{\Psi} \frac{K-1}{K} + \overline{U} \right] \frac{I}{\tau} \tag{23}$$

or

$$V_0 \frac{d}{d_0} \frac{\tau}{I} - \overline{U} = \overline{\Psi} \frac{K-1}{K}. \tag{24}$$

This equation will be satisfied by the experimental results if the ether is at rest. The quantity $\overline{\Psi}$ is given by equation (4), $\overline{B}$, the average value, for a current of one ampère, of the axial induction, being substituted for $B$.

If the ether and matter move together with the same velocity, the equation

$$V_0 \frac{d}{d_0} \frac{\tau}{I} - \overline{U} = \overline{\Psi} \tag{25}$$

will be satisfied. This assumes that the rotation takes place in vacuo, or that the surrounding air is not set into motion by the rotating parts. On the theory of Lorentz it is of no consequence whether the air moves or not, $K - 1$ for air being entirely neglible.

The experimental methods of determining all the quantities involved are described below.

### The Apparatus Used in the Principal Experiment.

A considerable portion of the apparatus was briefly described in explaining the general method used in the experiments. The bobbin on which the coil *C*, Fig. 3, was wound was made of a brass tube *D*, 48.0 cm. long, 16.5 cm. external diameter, and 1.6 mm. thick, and two thick brass rings about 30 cm. external diameter and of internal diameter equal to the external diameter of the tube. One side of each ring was turned plane, and the rings were mounted and soldered with their true surfaces outward, parallel, and flush with the ends of the tube. The true surfaces were then perpendicular to the axis of the tube.

The brass tube *H*, with internal diameter 11.8 cm., 48.0 cm. long, and 1.2 mm. thick, was made coaxial with *D* by means of two circular brass rings fitting tightly between the tubes near the ends. The tubes and rings were heavily soldered together. Small brass tubes soldered through the rings near their tops permitted a stream of tap-water to flow, at the will of the observer, through the space between the brass tubes.

The coil *C* contained nearly 300 lbs. of No. 10 copper wire wound in two sections, each of approximately $26 \times 75$ turns. The sections were well insulated and screened from one another and from the bobbin. The coil was mounted in two heavy clamps with its axis horizontal in a north and south line. In Fig. 5, which is a diagram of the apparatus as seen from the S. end, corresponding to the right end of Fig. 3, one of the clamps is shown. *B* and *C* are heavy wooden blocks, cut out to fit the coil, and drawn together by brass bolts *DD*.

The bearings *EE* were cast from the non-magnetic alloy known as "lumen" metal, between which and bronze the friction is very slight. These castings were planed on their inner surfaces and the central portions of their outer surfaces, and were drilled with $\frac{7}{8}$ in. holes, accurately perpendicular to the plane surfaces. They were then so mounted in the large brass rings by small steel screws that the centers of the holes were on the axis of the brass tubes already described. The central portions of the bearing castings were 3.2 cm. thick.

Three rotors were used in the course of the motional experiments.

The cylinder $G$ is now insulated and connected to the electrometer, and $F$ is earthed. The charge $q'$ is distributed over the insulated system, and the electrometer gives a deflection $d_0$ proportional thereto by the constant $C$ of equation (20). Thus

$$q' = Cd_0 = -q_0 \frac{S'}{S'' + S'} = -V_0 \frac{S''S'}{S'' + S'}. \tag{21}$$

Dividing the equation (20) for $Cd$ by the equation (21) for $Cd_0$, and multiplying by $V_0$, we obtain

$$\frac{d}{d_0} V_0 = \frac{K-1}{K} \Psi + U. \tag{22}$$

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Thus equation (22) may be written

$$V_0 \frac{d}{d_0} = \left[ \overline{\Psi} \frac{K-1}{K} + \overline{U} \right] \frac{I}{\tau} \tag{23}$$

or

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This equation will be satisfied by the experimental results if the ether is at rest. The quantity $\overline{\Psi}$ is given by equation (4), $\overline{B}$, the average value, for a current of one ampère, of the axial induction, being substituted for $B$.

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Three rotors were used in the course of the motional experiments.

The first was turned from a phosphor bronze casting, and was shaped much like *B* in Fig. 3. The terminal portions were turned with great precision to fit the $\frac{7}{8}$ in. holes in the bearing castings *EE*. The central cylinder was also turned with great precision. Its length was 33.6 cm., within $\frac{1}{15}$ per cent., and its mean diameter was 5.044 cm. This mean was obtained from two readings at right angles on each of 13 circles equally spaced along the cylinder, the average departure of a single reading from the mean being much less than 0.001 cm. The ebonite rings *PP* were turned carefully, so that the possible longitudinal motion of the rotor was very slight. The middle of the central cylinder of the rotor was 23.5 cm. from the S. bearing, 0.5 cm. from the center of the bobbin. At the N. end of the rotor was a small cylindrical projection onto which was forced a brass cylinder. A large thread was turned in this to form a worm.

The second rotor was turned from a rod of Tobin bronze, which is far superior to phosphor bronze, with precision about the same as that of the first. The central cylinder had practically the same length as that of the first rotor, and a mean diameter nearly the same, viz., 5.045 cm. The center of this cylinder, like that of the first rotor, was 23.5 cm. from the S. bearing when in position. A worm was cut directly in the end of the N. terminal cylinder, which was longer than that of the first rotor.

The third rotor was a modification of the first, and will be described in connection with the experiments in which it was used.

When in position, the worm at the end of the rotor geared with a brass worm-wheel having 100 teeth. Once every hundred revolutions of the rotor a pin projecting from this wheel closed an electric circuit including the electromagnet of a chronograph. This arrangement, together with a standard clock, enabled the rotor's speed to be determined with precision.

The induction tube, or guard cylinder *G*, was a brass tube 36.4 cm. long, 8.70 cm. in external diameter, and 0.08 cm. thick.

The mechanism by which the wire *N*, connected with the rod *J*, Fig. 3, was operated is shown in Fig. 5. One end of a brass spring *I*, fastened at the other end to a nail in the wooden clamp *BC*, is attached to the cross-piece *H* near its upper end. To the same

point of *H* is attached one end of a cord *J*, which passes through a ring *M* and is attached near its other end to a small brass weight *K*. Below the weight are three small wooden steps. The spring, cord, and steps are so adjusted, that when the weight is on the highest, or first step, the string is loose and the spring presses the wire *N* (Fig. 3) gently against the tube *F*. When the weight is placed on the third step, *N* is raised above the tube *G*, into, or nearly into, contact with *H* (Fig. 3).

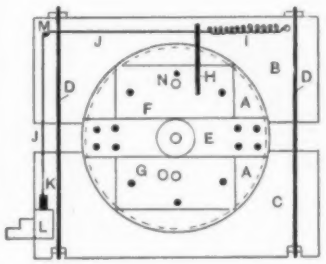


Fig. 5.

The essential parts of the keys 1, 2, 3, 4 in the final work were constructed throughout of brass and amber. Keys 1, 2, and 3 were very nearly alike. The principle is the same as that of the electrometer key described by McLennan at the Philadelphia meeting of the American Physical Society (December, 1904), but the keys described here are, in my opinion, much superior to McLennan's in insulation, simplicity of construction, and regularity in making and breaking contact. The construction of the keys is illustrated in Fig. 6. *B* is a rectangular block of amber about

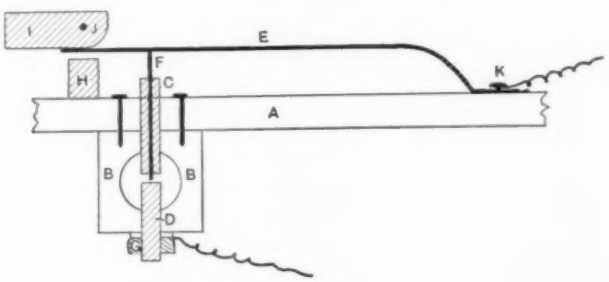


Fig. 6.

2.5 cm. × 2.5 cm. × 1 cm. A hole about 1.3 cm. in diameter is drilled through the center of the block from face to face. Smaller holes are drilled and threaded to hold the threaded brass rods *C* and *D*. The lower rod *D* is left solid, with a flat top, and is provided below with one or more nuts and washers for electrical connections. The upper rod *C* is drilled throughout its length to permit the

passage of a straight brass wire *F*, and the sharp edges of the hole are removed. The amber block is screwed beneath the top, or on one side, of a brass-lined box with the tube *C* projecting through a hole, which may be small or large according to purposes of the key. The tube *C* serves only as a guide to the wire *F*, and in some cases to complete the electric screening. The wire *F* is soldered at right

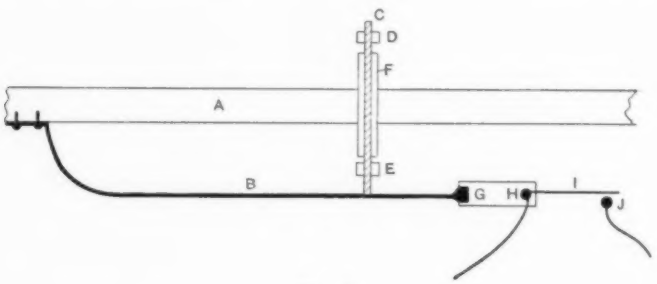


Fig. 7.

angles to a long brass strip *E*, which is bent as shown in the figure and screwed to the top of the box. The key is operated by the device *HIJ*, made of small pieces of wood and a small nail *J*. When *I* is made horizontal, *F* rises to its highest position, its lower end being then, if desired, within the tube *C*, and contact with *D* is broken. When *I* is made vertical, *F* is pressed down and makes contact with *D*. *I* remains in the position in which it is placed. The actual amber blocks used in the experiments described here were nearly twice as thick as those described above and their central portions were cut down to a thickness of about 1 cm. This shape, however, is inferior, on account of both insulation and expense, to the simpler shape illustrated in Fig. 6.

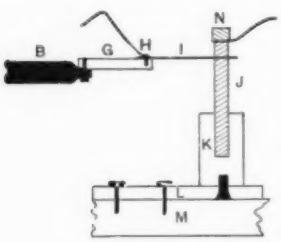


Fig. 8.

The construction of key 4 is shown in Figs. 7 and 8. A brass strip *B*, similar to those used in keys 1, 2, and 3, is screwed at one end to the under side of the top of the key box. The other end is screwed to one end of a small oblong block *G* of amber. A fine spring brass wire *I* is fastened to the other end of the amber block

by means of a screw *H*, which connects *I* to a fine brass wire running to the lower terminal of key 1. When *B* is lowered, the wire *I* makes contact with a brass rod *J*, and hence, by a fine brass wire, with the lower terminal of the electrometer key 3. The rod *J* is supported by an amber block *K* screwed to the brass plate *L*, itself screwed to one side of the key box *M*. The strip *B* is raised and lowered by means of the brass rod *C*, which is threaded and carries two brass nuts *D* and *E*. The rod moves vertically through the brass tube *F*, passing through the top of the box, the distance through which it moves and the position it occupies when *I* makes or breaks contact with *J* being regulated finely by the nuts *D* and *E*. Friction retains the rod *C* in either position in which it is set.

The keys 1, 2, 3, 4 were mounted in and on a brass-lined key box *E*, Fig. 9. The box contained also a commutator *ABCD*. It

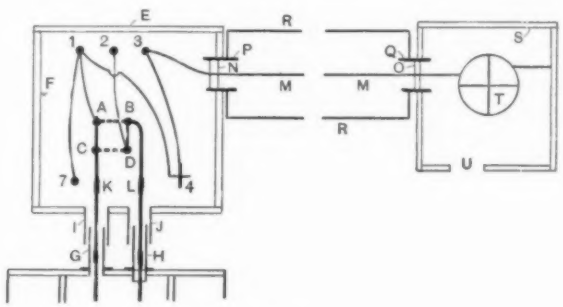


Fig. 9.

was made of a block of amber about 5 cm. × 5 cm. × 2.5 cm., four brass posts *A*, *B*, *C*, *D* screwed into the amber at the corners of a square, with two vertical saw cuts at right angles in the top of each, and two thin strips of brass by which the connections were made. It was mounted on a short pillar of brass, itself on a brass plate by which it was clamped to the base of the key box. This box was fastened to a heavy wall shelf which projected over the edge of the table supporting the great coil. The diagram shows roughly the relative positions of the keys, coil, etc., together with the electrical connections with the lower terminals of keys 1, 2, and 3. The posts *C* and *B* of the commutator were connected by the jointed brass rods *K* and *L* with the brass tube *G* and the rod *J*, of Fig. 3,

respectively. The rod $K$ passed through a brass tube $I$, projecting through the side of the box, and a considerably smaller brass tube $G$, telescoping with $I$, screwed to the upper brass plate closing the space within the great coil. The space between $I$ and $G$ was partially filled with cotton wool. The joint was sometimes covered with tin foil. The rod $L$ passed through a similar arrangement of brass tubes, cotton, and tin foil. This arrangement prevented the transmission of any vibration from the motor and rotating apparatus to the key box, and at the same time formed a perfect electric screen and prevented the rapid escape, by this channel, of dry air within the box.

The electrometer was mounted in a brass-lined box $S$, Fig. 9, screwed to a firm wall shelf. The boxes $E$ and $S$ were about 1.7 m. apart and were connected by the brass tubes $P$, $Q$, and $R$. Narrow pieces of amber $N$ and $O$ were screwed in $P$ and $Q$ along diameters, and a fine brass wire $M$, connected at one end with the lower terminal of key 3 and at the other with the electrometer, was stretched, but not tightly, between them. The electrometer was an instrument of the Dolezalek type, with amberoid insulation, by the Cambridge Scientific Instrument Company. It was modified in the instrument shop, a charging key being added, and two of the quadrants being made adjustable radially for symmetry. The needle furnished with the instrument by the makers was injured and it was replaced by one made in this country, for the earlier observations. The needle was magnetic, a fact which was very troublesome until the instrument was removed to a considerable distance from the coil. Its behavior was improved by substituting a wooden rod for the aluminium rod and vane originally carrying the mirror. The method of experiment entirely eliminated any error due to the residual deflection of the needle by a magnetic field, as the fields were always destroyed many seconds before the deflection was read. The mirror was slightly convex, and gave excellent definition with the telescope and 2 mm. scale used in the greater part of the work. In the experiments of 1908 an excellent new Cambridge needle, with the old mirror, was used. The telescope and scale were mounted on a pier, the scale being about 4.2 m. from the mirror. Tenths of divisions were easily estimated with certainty on

the 2 mm. scale; on a mm. scale used chiefly in the earlier part of the work they were estimated without great certainty. Several quartz fibers, varying in diameter from about $6\mu$ to about $9\mu$, were used in the course of the work. The needle was charged, through the key, to a potential of about 150 volts by means of a water battery.

The current which traversed the great coil in the principal experiment was supplied by a dynamo in the electrical engineering laboratory. By a simple arrangement of two switches the two sections in which the coil was wound could be connected either in parallel or in series. The terminals of this arrangement were connected through a reversing switch directly to the switchboard and dynamo mains. The capacity of the current meter, an excellent Siemens and Halske volt-ammeter, properly tested in this laboratory, was not sufficient to measure the total current when the two sections were in parallel; hence it was placed in one of the coil circuits through a reversing switch, and the resistances of the two coil circuits were made the same. The ammeter was on the pier with the telescope, so far from the coil as not to be affected by its field. Owing to the large amount of power consumed in the coil when its two sections were in parallel, many seconds elapsed after closing the circuit before the current reached an approximately steady value. In a single experiment the current was required for 30$^s$, but its value had to be known with accuracy only at the end of this time, just before insulating the tube $G$ (see above); for only the part of the charge due to electric absorption could be affected by the value of the current prior to the instant mentioned. The ammeter was therefore read at this instant.

In the earlier experiments the rotor was usually driven by belt from a 1 h.p. direct current shunt-wound motor. The same dynamo supplied power to this motor and to the great coil — an objectionable arrangement, but the only one practicable. The speeds, however, were in almost all cases quite sufficiently constant. Different speeds were obtained by using different pulleys and an adjustable rheostat. In the later work a 2 h.p. alternating current motor was used, the constancy of whose speed left nothing to be desired.

## THE MAGNETIC FIELD OF THE GREAT COIL.

In order to obtain the quantity $\overline{V}$ and one of the quantities constituting $\overline{U}$, viz., the value of $V'$ for a current of 1 ampère in the coil, or $\overline{V}'$, a study of the magnetic field throughout the region occupied by the rotating insulator and its metal cover was necessary. The well known method of the test coil, mutual inductance standard, and ballistic galvanometer was used, all necessary care being taken to secure more than adequate precision. The test coils were wound on true brass cylinders from No. 40 SSC. copper wire. Each coil contained from 40 to 42 turns, and was coaxial with the rotor when under experiment. Table I. gives the flux in electromagnetic C.G.S. units through the mean turn of each coil, for a current of 1 ampère in the great coil, as a function of its distance in cm. from the S. end of the bobbin. For each coil a smooth curve was plotted on a large scale between the flux and the distance. From each curve the flux through the mean turn of the corresponding coil was obtained for intervals corresponding to every half cm. of the length of the central cylinder of the rotor; and from these and the necessary additional curve readings, corresponding to points near the ends of the central cylinder, the mean flux through the mean turn was calculated for the whole distance between the ends of the central cylinder. The mean flux thus

TABLE I.

*Magnetic Field of Great Coil. July* 25, 1907.

| Coil 1. | | Coil 2. | | Coil 3. | | Coil 4. | |
|---|---|---|---|---|---|---|---|
| Distance. | Flux. | Distance. | Flux. | Distance. | Flux. | Distance. | Flux. |
| 6.2 | 1418 | 6.2 | 1770 | 5.2 | 1989 | 4.2 | 2491 |
| 7.2 | 1492 | 9.2 | 2007 | 9.2 | 2365 | 7.2 | 2926 |
| 10.2 | 1652 | 12.2 | 2142 | 12.2 | 2560 | 10.2 | 3258 |
| 13.2 | 1756 | 15.2 | 2225 | 15.2 | 2658 | 13.2 | 3476 |
| 16.2 | 1824 | 18.2 | 2269 | 18.2 | 2704 | 16.2 | 3557 |
| 19.2 | 1838 | 21.2 | 2276 | 21.2 | 2717 | 19.2 | 3588 |
| 22.2 | 1839 | 24.2 | 2268 | 24.2 | 2698 | 22.2 | 3593 |
| 25.2 | 1831 | 27.2 | 2255 | 27.2 | 2687 | 25.2 | 3582 |
| 28.2 | 1817 | 30.2 | 2228 | 30.2 | 2657 | 28.2 | 3575 |
| 31.2 | 1793 | 33.2 | 2178 | 33.2 | 2606 | 31.2 | 3518 |
| 34.2 | 1732 | 36.2 | 2084 | 36.2 | 2473 | 34.2 | 3416 |
| 37.2 | 1651 | 39.2 | 1932 | 39.2 | 2288 | 37.2 | 3232 |
| 40.2 | 1496 | 42.2 | 1682 | 42.2 | 2008 | 40.2 | 2934 |

determined for each coil is given in Table II. This table also gives the mean diameter of each coil and the ratio of the mean flux through its mean turn to the cross-section of this turn, *i. e.*, the mean magnetic induction parallel to the axis of the rotor through the turn. The results show that the mean flux across a right section of the insulating cylinder, its coat, or the rotor, is proportional to the area of this section, and equal to that area × 88.65 in C.G.S. electromagnetic units.

TABLE II.

| No. of Test Coil. | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Mean diameter of coil. | 5.009 cm. | 5.571 | 6.081 | 7.011 |
| Mean flux through mean turn. | 1746 | 2162 | 2573 | 3425 |
| Mean induction through mean turn. | 88.6 | 88.7 | 88.6 | 88.7 |

Mean induction through mean turns of all four coils $= \bar{B} = 88.65$.

## THE MEAN POTENTIAL OF THE CENTRAL SURFACE OF THE ROTOR FOR A CURRENT OF 1 AMPÈRE IN THE GREAT COIL.

Owing to lack of symmetry and to the extension of the bearing surfaces currents exist to some extent in the rotor. Hence the quantity sought cannot be obtained precisely from a knowledge of the magnetic field. An approximately correct value can be obtained by determining the mean magnetic flux through the tubular bearing surfaces experimentally by means of a suitable test coil, etc., and subtracting this from the mean magnetic flux across a right section of the central cylinder of the rotor, obtained from its diameter and Table II. Near the close of the work described here this was carefully done, and the value 1,613 C.G.S. units obtained. This is nearly the same as the more nearly correct value found earlier by the following method :

The brass bearing *K*, Fig. 3, was replaced by a bearing of ebonite, and the rod *JJ* by a long brass rod of the same diameter marked in cm. Fastened to the rod at a known point was a narrow strip of brass *A* with its plane vertical and perpendicular to the rod. *A* was kept pressed against the rotor by means of a cross-piece and a small weight, and could be made to touch the rotor at any desired distance from the S. end of the bobbin. The rotor was driven very uniformly, and almost continuously through-

out a series of observations, by a storage battery, which furnished current at the same time to the great coil. The current was measured with the volt-ammeter already mentioned, and the potential $v'''$, or the voltage from the point of contact of $A$ and the rotor to the earthed bobbin, was measured with a D'Arsonval galvanometer,

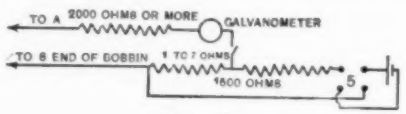


Fig. 10.

etc., the apparatus being arranged as in Fig. 10. The battery shown in the figure was of course used only for calibration purposes. Speeds were recorded automatically on the chronograph.

Two series of observations were taken on rotor 1. The resulting values of $\bar{v}'''$, or $v'''$ for a current of 1 ampère in the great coil and a rotor speed of 1 revolution per second, in C.G.S. units, are given as a function of the distance $D$ in cm. from the S. end of the bobbin in Table III. The average value of $\bar{v}'''$, or $\bar{V}'''$, for the central

TABLE III.

| First Rotor. June 17, 1907. | | | | Second Rotor. December 3, 1907. | |
|---|---|---|---|---|---|
| $D$ | $\bar{v}'''$ First Series. | $\bar{v}'''$ Second Series. | $\bar{v}'''$ Mean. | $D$ | $\bar{v}''$ |
| 7.6 | 1390 | 1385 | 1388 | 7.1 | 1372 |
| 8.6 | 1444 | 1440 | 1442 | 8.2 | 1416 |
| 10.6 | 1551 | 1544 | 1548 | 9.2 | 1479 |
| 12.6 | 1615 | 1613 | 1614 | 11.2 | 1569 |
| 14.6 | 1658 | 1662 | 1660 | 13.2 | 1629 |
| 16.6 | 1690 | 1679 | 1684 | 15.2 | 1679 |
| 18.6 | 1703 | 1701 | 1702 | 17.2 | 1703 |
| 20.6 | 1702 | 1702 | 1702 | 19.2 | 1711 |
| 22.6 | 1715 | 1713 | 1714 | 21.2 | 1714 |
| 24.6 | 1702 | 1705 | 1704 | 23.2 | 1698 |
| 26.6 | 1700 | 1700 | 1700 | 25.2 | 1703 |
| 28.6 | 1687 | 1691 | 1689 | 27.2 | 1695 |
| 30.6 | 1678 | 1673 | 1676 | 29.2 | 1694 |
| 32.6 | 1643 | 1638 | 1640 | 31.2 | 1665 |
| 34.6 | 1595 | 1603 | 1599 | 33.2 | 1635 |
| 36.6 | 1541 | 1545 | 1543 | 35.2 | 1588 |
| 38.6 | 1457 | 1470 | 1464 | 37.2 | 1523 |
| 40.1 | 1336 | 1358 | 1347 | 39.2 | 1448 |
| | | | | 40.2 | 1389 |

surface of rotor 1 was 1,616 C.G.S. units, each series giving the same result. The results of a similar series of observations on rotor 2 are given in the same table. From this series $\bar{V}'''$ for rotor 2 is 1,620 C.G.S. units. An earlier, but inferior, set, obtained under adverse conditions, gave 1,617 C.G.S. units. Within the limits of experimental error these values are all identical; and as the differences between the diameters, lengths, and positions of the central surfaces of the two rotors were neglible, the mean of the first and second results, viz., $\bar{v}''' = 1{,}618$ C.G.S. units, or 0.00001618 volt, will be adopted for both rotors.

It was also found by experiment that the voltage between the two ends of the great bobbin was less than one sixth per cent. of the potential of the center of the central surface of the rotor.

## Determination of the Dielectric Constants.

To determine the dielectric constant of the insulator $A$, the rod $J$ was connected with the lower terminal of key 1, and the tube $G$ with that of key 2, Fig. 11, the change from the arrangement used in the experiment proper being made by means of the commutator $ABCD$ of Fig. 9. Also the lower terminal of key 1 was connected to the "charge," or lower, terminal $A$ of a Kempe key 6, the upper terminal $B$ of which was earthed. The lever of the key was connected with one armature of a standard mica condenser $C$, whose other armature was earthed.

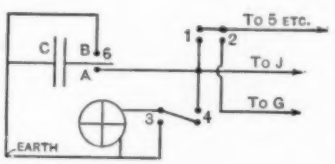

Fig. 11.

In the determination of a dielectric constant two series of operations were necessary. (1) The resistance $R$, Fig. 3, was given a considerable value $R_1$. Initially keys 1, 2, and 3 were closed, $N$ down, 4 and 5 open, and the lever of 6 up. Then, in succession, (*a*) 5 was closed, (*b*) $N$ was raised, (*c*) 5 was opened, (*d*) 1 was opened, (*e*) 4 was closed, (*f*) the lever of 6 was lowered, (*g*) 3 was opened, (*h*) $N$ was lowered, and the electrometer scale reading was taken. The process was repeated with the commutator 5 reversed, and the double deflection $d_1$ was obtained. In each of these processes the condenser $FAB$ was first charged to a voltage $V_1 = R_1 I$ ($I$ being

the constant current in the circuit $RST$). The field of this condenser, surrounded by the guard tube $G$ at the same potential as its outer coat, was essentially a straight-line field confined to the dielectric $A$. Then the conductor $F$ was connected to the insulated terminal of the standard condenser $C$, and the combination was then connected with the electrometer, $G$ and all other conductors being earthed.

(2) The resistance $R$ was given a much smaller value $R_2$, while the total resistance $R + S$ was kept the same as in (1). Initially 1, 2, and 3 were closed, 4 and 5 open, $N$ down, and the lever of 6 down. Then, in succession, (*a*) the lever of 6 was thrown to "insulate," (*b*) 5 was closed, (*c*) the lever of 6 was lowered, and (*d*) then immediately raised to "insulate," (*e*) 5 was opened, (*f*) 1 was opened, (*g*) 4 was closed, (*h*) 3 was opened, (*i*) the lever of 6 was lowered, and the electrometer reading was taken. The process was then repeated with the commutator 5 reversed, and the double deflection $d_2$ was obtained. In each of these processes the standard condenser was first charged to a voltage $V_2 = R_2 I$, and its insulated terminal then connected to the conductor $F$, all the conductors at the end of process (2) being connected precisely as at the end of process (1).

The double deflections of the electrometer in (1) and (2) are proportional to the charges on the insulated conductors. The charge in (1) is very approximately $S' V_1$. The charge in (2) is $S_2 V_2$, if $S_2$ denotes the capacity of the standard condenser. Thus

$$\frac{d_1}{d_2} = \frac{S'' V_1}{S_2 V_2} = \frac{S'' R_1}{S_2 R_2},$$

or

$$S'' = S_2 \frac{d_1}{d_2} \frac{R_2}{R_1},$$

from which $S''$ can be readily determined. The dielectric constant $K$ can then be obtained from $S''$ and the dimensions of the cylinder $A$. If $r_1$ and $r_2$ are the internal and external radii of this cylinder, and $l$ its length, we have

$$K = S'' \frac{2 \log r_2/r_1}{l}.$$

The capacity $S''$ is slightly greater than that of the straight-line field Hence $K$ as determined above will be slightly too large. An error in $K$, however, makes a much smaller error in $K - 1/K$, the quantity with which we are concerned, since $d/dK[(K-1)/K] = 1/K^2$.

The condenser used in the earlier experiments in sulphur, ebonite, and rosin, was the 0.02 M.F. division of an Elliott 1 M.F. mica condenser. The capacity of this division was compared with that of each higher division, from 0.05 M.F. to 0.50 M.F., by charging each to a voltage inversely proportional to its nominal capacity, and measuring the resulting throw on discharging through a ballistic galvanometer. The throw produced by the 0.02 M.F. division was 4.79 cm., which is just equal to the mean of the throws produced by the other divisions.

In order to secure higher insulation than could readily be obtained with the Elliott condenser, with external insulation of ebonite and paraffin, it was replaced, in the later work, by a condenser constructed according to my design by Messrs. Leeds and Northrup. This is a mica condenser with air and amber external insulation. The terminals of the armatures are insulated by amber pillars, petticoated at the bottom, and fastened through the top of a small brass box. This condenser also failed to insulate sufficiently under conditions prevalent here; but it was made to insulate excellently by perforating the brass box with numerous holes, inserting all but the top in a larger paraffin-soaked wooden box whose bottom was covered with calcium chloride, and sealing up with beeswax. To increase the insulation still further, the condenser was ordinarily kept, while in use, within a large box heated to a temperature considerably higher than that of the room. The capacity of this condenser was certified by the makers to be 0.02 M.F., according to their own standard, within one fourth per cent. It did not differ by as much as one sixth per cent. from that of the Elliott condenser previously used.

The key 6 used in the earlier work was a Kempe key in ebonite and brass by Elliott. For the later work this key was modified in the instrument shop of this laboratory. The ebonite was replaced throughout by amber and brass, the insulation of amber being much superior to that of ebonite.

Connection between key 6 and key 1 was made by fine brass

wires $G$ and $H$ and the other apparatus shown in Fig. 12. The brass tube $A$ passed through a hole in the top of the key box, and was held in position by a small ring $B$. It held in position a tube of amber $FF$, to the bottom of which was screwed a brass plate $E$. During experiments on capacity, a slender brass binding post $D$ was kept screwed into the middle of the plate $E$. Except when capacity measurements were in progress, the rod $D$ was removed and the cylinder $A$ was covered with a brass cap $C$.

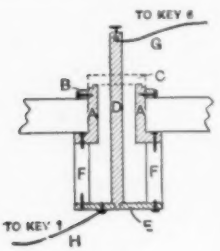

Fig. 12.

## The First Experiments on Sulphur.

The sulphur used for the first cylinder which was successfully prepared was of the grade known as "washed sulphur." A rough cylinder of this material was cast in a cylindrical mold on the first bronze rotor, and this cylinder was accurately turned up on a lathe. It was covered with a thin coat of brass in the following manner, at the suggestion of Professor Stratton and Mr. Lange, of the National Bureau of Standards, accidents having interfered with the success of the electroplating process used later in coating a number of other cylinders with copper, and with another electrolytic process. A very uniform brass tube, whose internal diameter was about the diameter desired for the sulphur cylinder, not yet turned, was pounded onto an accurately turned cylinder of steel, prepared for the purpose. The average departure of 13 diameters of this cylinder from their mean was much less than 0.001 cm. The steel cylinder was then mounted in a lathe, and the brass coat was turned down until about 0.025 cm. thick. The brass coat was then heated and slipped off the steel cylinder. The sulphur cylinder was turned to a diameter about 0.002 cm. less than that of the steel. The brass tube was then forced onto the sulphur cylinder. In this process the rotor and sulphur cylinder were bent, but they were very approximately straightened by Mr. Lange, with great skill, in a heavy drill press. The rotor was then mounted in a lathe, the brass tube and sulphur cylinder were cut off at the proper points, and the brass tube was turned down until its mean external diameter

was 6.832 cm. The precision of the turning was as great as in the case of the sulphur cylinder, whose mean diameter, obtained from 26 properly spaced readings, was 6.802 cm., the average departure of a single reading from the mean being much less than 0.001 cm. The difference between 6.832 cm. and 6.802 cm. would give 0.015 cm. as the thickness of the brass coat. After the experiments were completed this thickness was studied more carefully. The brass coat was removed and cut into 11 strips, each about 3 cm. wide. The thickness of each of these strips, which were about 21.4 cm. long, was measured at 7 points about 3 cm. apart. The mean thickness obtained in this way was 0.0156 cm. Each strip gave nearly the same mean, the variations being about 0.001 cm. But the mean thickness along one generating line of the cylinder was 0.011 cm. (the minimum), and that along an almost diametrically opposite generating line was 0.022 cm. (the maximum). Thus the axis of the outer surface of the coat was parallel to that of the inner surface, the rotor, etc., but was slightly displaced laterally therefrom. The departures from the theoretical conditions of the experiments could have had no appreciable effect on the results even had the work been of far greater precision.

The dielectric constant of the sulphur was measured by the process described above. The manner in which this constant depended upon the time of charging was first investigated by repeating process (1) for a number of different times of charging, from 1 second to 40 seconds. The capacities and dielectric constants were approximately proportional to the electrometer throws given in the following table :

| Time in seconds : | 1 | 10 | 20 | 30 | 40 |
|---|---|---|---|---|---|
| Mean electrometer throw : | 11.25 | 11.36 | 11.38 | 11.43 | 11.42 |

The results show that absorption is practically complete after 30$^s$ at most. This fact being known, the dielectric constant was determined by a series of the processes (1) and (2), performed alternately to eliminate a possible change in the electrometer's sensibility, the time of charging in (1) being 30$^s$. The values of $R_1$ and $R_2$ were 5,000 ohms and 50 ohms, respectively. The results are given in the following table :

| Process: | (2) | (1) | (2) | (1) | (2) |
|---|---|---|---|---|---|
| Mean throw: | 8.80 | 10.70 | 8.80 | 10.69 | 8.81 |

The ratio of the mean throw for process (1) to that for process (2) is 1.215, that of $R_1$ to $R_2$, 100. Together with the dimensions of the sulphur cylinder, these data give for the dielectric constant

$$K = 3.89 \text{ for the time of charging } 30^s.$$

The process of "calibration" was carried out as follows: Initially keys 1, 2, 3 were closed, $N$ down (in contact with $F$), and 4 and 5 open. Then, in succession, ($a$) 5 was closed, ($b$) $N$ raised, ($c$) 5 opened, ($d$) 1 opened, ($e$) 4 closed, ($f$) 3 opened, ($g$) $N$ lowered, and ($h$) the electrometer scale reading taken. The process was then repeated with 5 reversed, and again with 5 in its original position. The double deflection $d_0$ corresponding to the voltage $V_0$ along $R$ was obtained. In this process, all the operations, with a few exceptions, were performed in quick succession. In ($a$), 5 was kept closed for $30^s$; in ($f$) 3 was opened $30^s$ after $N$ was raised in ($b$), except in the earlier experiments, when this interval was $20^s$; and the electrometer reading in ($h$) was ordinarily taken $70^s$ after the opening of 3 in ($f$). The $20^s$ or $30^s$ interval between ($b$) and ($f$) was determined on from a series of experiments in which this interval was varied from $5^s$ to $30^s$. The electrometer *throws* increased from 11.66 for $5^s$ to 11.76 for $15^s$ to $30^s$.

In the experiment proper, keys 1 and 5 were initially open, 2, 3, 4 closed, $N$ down, the rotor at rest, and the current in the coil zero. Then, in succession, $N$ was raised, the motor was started and brought to full speed, the coil circuit was closed, the current was determined, 3 was opened $30^s$ after the coil circuit was closed, the coil circuit was broken, the motor was stopped, $N$ was lowered, and the electrometer scale reading was taken, ordinarilly $70^s$ after 3 was opened. The process was repeated with the coil current reversed, and again with the current in the original direction. The double deflection $d$ corresponding to the coil current $I$ and the period $\tau$ of the rotor was determined. All operations were performed in quick succession, except as indicated.

In both sets of experiments the double deflection of the electrometer was obtained by taking the difference between the second

reading and the mean of the first and third. In most cases four or more readings were taken instead of three, deflections being alternately in opposite directions. In such cases the same mode of combination was followed. Thus, in the case of four readings, the first and third were combined with the second, and the second and fourth with the third; and the mean of the two double deflections was taken. All observations were taken at regular intervals, the times being recorded. The quotient of the current and the period of the rotor was treated like the electrometer deflection in combining observations. In case a single observation had to be rejected, the two preceding and the two following were combined. A few observations were rejected because the wire $N$ was accidentally left or put in contact with the tube $F$ while the rotor was in motion, which caused fine particles of metal to fly off from $N$ and $F$ to $G$, or because particles flew off for other reasons. In this way large deflections, entirely different from those due to the effect in question, were produced.

As the sensibility of the electrometer did not remain constant throughout a series of observations, the "calibration" was performed a number of times during each series of observations, for a known value of $V_0$; and from these observations a curve was plotted between $d_0$ and the time, from which $d_0$ was obtained for any time for which it was needed. In no case was the average departure of the experimental value of $d_0$ from the value given by the curve less than about one half per cent. or greater than about three fourths per cent.

The mean values of $\tau$, $I$, $d/d_0 \cdot V_0$, $I/\tau$ and $d/d_0 \cdot V_0 \cdot \tau/I$ for each set of observations are given in Table IV. The table also gives the ranges of $d$ and $d_0$. The values of the quantities in the seventh and eighth columns were calculated as indicated above, and not from the values of $\tau$ and $I$ given in the table, which are simply the mean values for the sets, inserted to show the approximate values of the quantities in the different experiments. Owing to the large departures of the single observations of $d$ from their mean, these mean values of $\tau$ and $I$ could, of course, have been used in the calculations without serious effect. The mean value of $d/d_0 \cdot V_0 \cdot \tau/I$ given at the foot of the last column was obtained by multiplying

the numbers in each of the two columns immediately preceding by the number of observations in the set, adding in two columns, and dividing the sums of the numbers in the first column by the sum of those in the second.

TABLE IV.

*First Sulphur Cylinder. June* 10–14, 1907.

| No. of Set. | No. of Observations in Set. | $\tau \times 100$ in Seconds. | $I$ in Amperes. | $d$ in cm. | $d_0$ in cm. | $d/d_0 \cdot V_0$ in Volts. | $I\tau$. | $d/d_0 \cdot V_0 \cdot \tau/I$. |
|---|---|---|---|---|---|---|---|---|
| 1 | 7 | 1.435 | 12.15 | | | 0.0252 | 845 | 0.0000298 |
| 2 | 6 | 1.446 | 12.21 | | | 231 | 844 | 274 |
| 3 | 8 | 1.455 | 12.00 | | | 234 | 828 | 283 |
| 4 | 8 | 1.457 | 11.93 | | | 206 | 819 | 252 |
| 5 | 8 | 1.474 | 21.38 | From | From | 395 | 1453 | 272 |
| 6 | 4 | 1.472 | 20.63 | 1.58 | 6.24 | 381 | 1399 | 272 |
| 7 | 8 | 1.442 | 12.48 | to | to | 225 | 865 | 260 |
| 8 | 4 | 1.447 | 12.18 | 6.92 | 7.56 | 226 | 843 | 268 |
| 9 | 4 | 1.488 | 21.60 | | | 383 | 1450 | 264 |
| 10 | 6 | 1.471 | 21.06 | | | 384 | 1431 | 268 |
| 11 | 6 | 1.344 | 11.77 | | | 212 | 887 | 239 |
| 12 | 6 | 3.35 | 21.71 | | | 172 | 647 | 266 |
| 13 | 6 | 3.72 | 20.14 | | | 136 | 543 | 250 |
| 14 | 4 | 3.77 | 21.28 | | | 140 | 568 | 246 |
| 15 | 4 | 2.37 | 11.50 | | | 144 | 490 | 294 |
| 16 | 4 | 1.368 | 20.42 | | | 368 | 1496 | 246 |
| 17 | 10 | 1.288 | 11.27 | | | 227 | 878 | 259 |
| 18 | 4 | 1.305 | 20.10 | | | 408 | 1542 | 265 |
| 19 | 4 | 2.57 | 11.20 | | | 109 | 430 | 253 |
| 20 | 4 | 2.91 | 19.98 | | | 162 | 690 | 235 |

Weighted mean 0.0000264½

Average departure from mean 13

From the data given above, the value of $\Psi(K-1)/K$ for the sulphur cylinder is $0.00001450 \times 2.89/3.89$ volt $= 0.0000108$ volt, and the value of $U$ is 0.00001618 volt + 0.00000030 volt = 0.0000-1648 volt. Hence the mean value of $d/d_0 \cdot V_0 \cdot \tau/I - U$ is 0.0000100 volt, which differs from $\Psi(K-1)/K$ by between 7 per cent. and 8 per cent. This discrepancy is less, however, than the average departure from their mean of the values of $d/d_0 \cdot V_0 \cdot \tau/I$ for the separate sets, which is about 13 per cent. The theory of Lorentz is thus confirmed within the limits of the experimental error; while the discrepancy between the experimental results and those to be

expected on the ether motion theory is over 45 parts in 145, or over 31 per cent.

The constancy of the last column in the table shows that $d/d_0 \cdot V_0 - U$ is proportional to $I$ and inversely proportional to $\tau$, as required by all theories. The same thing is shown by Fig. 13, in

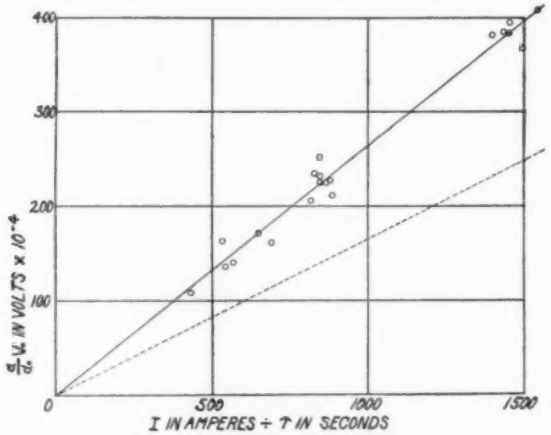


Fig. 13.

which the continuous line gives the relation between $d/d_0 \cdot V_0$ and $I/\tau$, and the dotted line that between $U$ and $I/\tau$. The full line is so drawn that the ratio of the ordinate of any point to its abscissa is the weighted mean 0.0000264½, and the separate sets of observations are indicated in the usual way.

In order to obtain sufficient insulation the room in which the experiments were performed was kept at a temperature considerably higher than that outside, and bottles of sulphuric acid were kept inside the key box and the electrometer box. For the same purpose, and also to remove dust from the chamber in which the rotor moved, a slow stream of air was driven into the inlet $I$ through a calcium chloride bottle and a cotton filter. This was kept up day and night by a hand bellows operated by a small motor.

### The First Experiments on Rosin.

A rough cylinder of rosin, of one of the lighter varieties, was cast on rotor 2, and was then turned up accurately in a lathe. Its length, like that of the central cylinder of the rotor, was 33.6 cm.

within $\frac{1}{16}$ per cent. and its mean diameter was 6.651 cm. from 12 measurements equally spaced along the cylinder, the average departure from the mean being 0.002 cm. The rosin cylinder, before being cut to the proper length, was covered with a thin sheet of copper by the well-known electrolytic process used in electrotyping. The rosin was first rubbed with powdered graphite. A thin sheet of copper was then deposited by sprinkling the surface with iron filings and rotating it in a solution of copper sulphate. After being washed, the copper coat was thickened by being made the kathode in a copper sulphate electrolytic cell whose anode was a circular cylinder of copper nearly coaxial with the rotor. After being electroplated, the cylinder was treated with emery paper and sand paper in a lathe and its ends trued to the rotor. After the experiments the copper coat was stripped off and weighed. From the weight and area of the sheet and the density of copper the mean thickness was found to be 0.025 cm.

TABLE V.

*First Rosin Cylinder. July* 23–24, 1907.

| No. of Set. | No. of Observations in Set. | $\tau \times 100$ in Seconds. | $I$ in Amperes. | $d/d_0 \cdot V_0$ in Volts. | $I/\tau$. | $d/d_0 \cdot V_0 \cdot \tau/I$. |
|---|---|---|---|---|---|---|
| 1 | 6 | 1.433 | 20.91 | 0.0352 | 1453 | 0.0000242 |
| 2 | 6 | 1.385 | 11.17 | 196 | 806 | 244 |
| 3 | 7 | 1.212 | 11.26 | 234 | 931 | 240 |
| 4 | 6 | 1.231 | 20.22 | 405 | 1641 | 247 |
| 5 | 4 | 1.503 | 12.06 | 177 | 801 | 220 |
| 6 | 4 | 1.420 | 11.91 | 189 | 839 | 225 |
| 7 | 5 | 1.463 | 21.49 | 356 | 1472 | 242 |
| 8 | 10 | 1.446 | 21.16 | 350 | 1458 | 240 |
| 9 | 4 | 1.187 | 20.00 | 426 | 1696 | 251 |

Weighted mean 0.0000242½
Average departure from mean 7

The dielectric constant of the rosin was determined in the same manner as that of the sulphur. Three sets of measurements each gave this constant as 2.99 for a charging time of 30 seconds.

The experiments on the motion of the rosin in a magnetic field was conducted in nearly the same manner as the corresponding experiments on sulphur. But instead of series of "calibration" ex-

periments, a series of determinations of the voltage sensibility was made on each of the two observation days; and the ratio of the "calibration" deflection to the voltage deflection for the same E.M.F. was determined once for all from a special series of observations. Also, the bellows was not operated, and heat was not supplied to the room, for a number of hours during the night. The cylinder was heated in the rotation chamber before the experiments began, the temperature being that of tap-water during the experiments.

The results of the observations are given in Table V., where the same symbols are used as in Table IV.

From the data given in this table and earlier, $\overline{U}$ is 0.0000166½ volt, and the mean value of $d/d_0 \cdot V_0 \cdot \tau/I - \overline{U}$ is 0.0000076 volt, with an

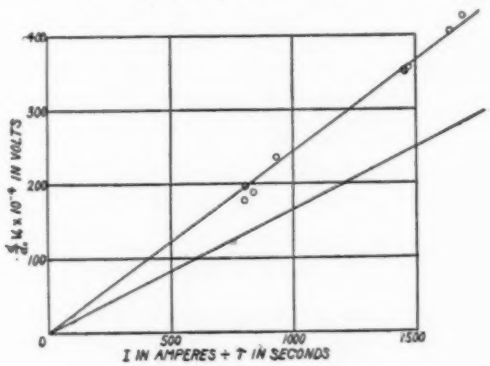


Fig. 14.

average departure from the mean of nearly 10 per cent. The quantity $\overline{\Psi}$ is 0.00001308 volt, and $\overline{\Psi}(K-1)/K$ is 0.000087 volt. The discrepancy between these experimental results and Lorentz's theory is thus 11 parts in 87, or nearly 13 per cent., and that between the experimental results and the alternative theory is 55 parts in 131, or 42 per cent. The experimental error is large, but the results are again decidedly in favor of the first-named theory.

Like the experiments on sulphur, those on rosin show a direct proportionality between $d/d_0 \cdot V_0 - U$ and the quotient $I/\tau$, as demanded by all theories. This is shown by the table, as also by the graphs of Fig. 14. The upper line shows the relation between $d/d_0 \cdot V_0$ and $I/\tau$, and the lower line that between $U$ and $I/\tau$.

### THE FIRST EXPERIMENTS ON EBONITE.

From a thick ebonite tube five hollow cylinders were turned, the sum of their lengths being made about equal to the length of the central cylinder of rotor I and their internal diameters about equal to the diameter of the same cylinder. These cylinders were forced into position on the rotor and the outer surface of the long ebonite cylinder thus formed was turned down to a mean diameter of 6.716 cm. This surface was then covered with a thin layer of shell-lac and a coat of silver leaf, after which the whole was heated inside the great coil. The dielectric constant of the ebonite was determined, and found to be 3.90. The variation of this constant with time of charging was also investigated. It was approximately proportional to the mean electrometer throws in the following table:

| Time of charging: | 10s | 20s | 30s | 40s |
|---|---|---|---|---|
| Mean throw: | 21.45 | 21.78 | 21.84 | 21.88 |

Experiments on the effect of the motion of the ebonite in the magnetic field of the great coil were begun, but the effect was found to be completely masked by another and much larger effect, independent of the magnetic field and the direction of rotation, and proportional to the square of the frequency of rotation. The effect was too great and too irregular to permit of its elimination in the magnetic experiments by taking observations with both directions of the magnetic field. The effect was such as would be produced by a radial E.M.F. acting outward in the ebonite during the rotation only and proportional to the square of the frequency, as if there were a centrifugal differential displacement of the two kinds of electrons.

The results of the first two series of systematic observations, during which the mean temperature was about 33° C., are given in Table VI.

### TABLE VI.

*Ebonite Cylinder.*

| June 25, 1907. | | | | | June 26, 1907. | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Time. | $S$ | $\tau \times 100$ | $S/\tau^2$ | $D$ | Time. | $S$ | $\tau \times 100$ | $S/\tau^2$ | $D$ |
| 3h 40m | 12.85 | 5.02s | $51 \times 10^2$ | 1.46 | 10h 17m | 9.58 | 1.924 | $259 \times 10^2$ | 7.75 |
| 3 56 | 12.76 | 3.92 | 83 " | 2.37 | 11 25 | 9.41 | 1.228 | 624 " | 21.0 |
| 4 14 | 12.71 | 3.60 | 98 " | 2.82 | 11 47 | 9.35 | 1.204 | 645 " | 21.7 |
| 4 36 | 12.65 | 2.16 | 271 " | 9.27 | 2 18 | 8.91 | 0.743 | 1614 " | 50.4 |
| 4 55 | 12.61 | 1.91 | 346 " | 11.97 | 2 40 | 8.84 | 0.861 | 1193 " | 41.2 |

The relation between the deflection ($D$) and the ratio of the electrometer's sensibility ($S$) to the square of the period ($\tau$) of the rotor is shown graphically in Fig. 15. This effect was studied on sev-

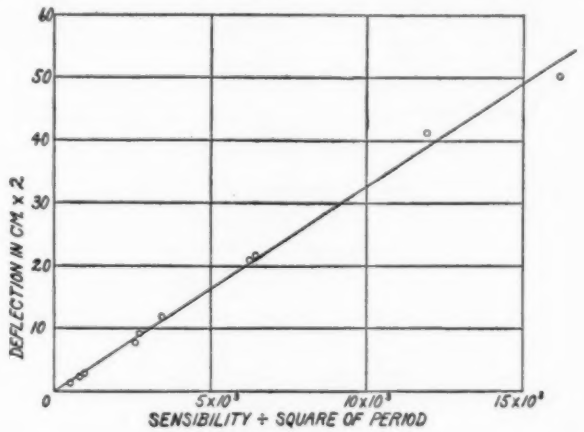


Fig. 15.

eral days. Its magnitude appeared to depend on the temperature of the ebonite and on other factors, no one of which has yet been sufficiently investigated.

The effect did not exist with the rotor alone, and it did not exist, in a later series of experiments, either with the rotor alone, or when an insulating cylinder of the usual dimensions but completely covered with copper in contact with the rotor was rotated.

### Experiments on Paraffin and Spermaceti.

A cylinder of pure hard paraffin was cast on one of the rotors turned true on a lathe, and covered with a copper coat by the electrolytic process already described. The electric absorption of the paraffin cylinder, as tested with an electroscope, was so great, however, that no further experiments were made with it. Doubtless a cylinder free from absorption could have been produced, had we been able to cast under pressure. But, having no facilities for this, we were unable, in several attempts, to get a homogeneous cylinder free from numerous cavities.

Attempts to cast on a rotor cylinders of paraffin and of spermaceti, at once homogeneous and firmly adherent to the rotor, having

failed, a mixture consisting of equal parts, by weight, of the two was tried. This also failed. A rough adherent cylinder of the mixture was finally formed by a dipping process similar to that by which the old fashioned tallow candle was formed. This was turned up and coated with copper in the usual way. The absorption of this cylinder, also, was very great. Nevertheless it would have been examined for the electrical effect in question, though without hope of quantitative results of value, had not it been injured by accident just as the experiments were starting.

### LATER EXPERIMENTS WITH SULPHUR.

A second cylinder of sulphur was cast on rotor 2, turned down to a mean diameter of about 6.934 cm., covered with a layer of paraffin 0.006 cm. thick, then covered with a coat of copper 0.046 cm. thick, and then turned down at the ends until the length of the cylinder was 33.6 cm. The object of the paraffin coat was to prevent the penetration of the copper sulphate solution, used in electroplating, into the sulphur cylinder.

The capacity $S''$ of the cylinder was found to be 207 E.S. units for a charging time of 30". This gives the dielectric constant (calculated on the assumption of a homogeneous dielectric) about 3.94 for the time 30". The absorption was investigated as in the case of the other sulphur cylinder. The capacity for different times of charging was approximately proportional to the throws in the following table:

| Time of charging : | 1" | 10" | 20" | 30" | 50" |
|---|---|---|---|---|---|
| Mean throw : | 11.63 | 11.73 | 11.76 | 11.84 | 11.85 |

No experiments on the electric displacement in the cylinder due to its motion in a magnetic field were practicable, as this effect, at speeds giving sufficient sensibility, was completely masked by an apparently "centrifugal" E.M.F. similar to that found in the experiments on ebonite, but in the opposite direction, the E.M.F. being directed *inward*, and more constant in time. The results of the observations taken on the last day on which experiments were made with the cylinder are given in Table VII. Each deflection ($D$) given is the mean from ten readings, and all deflections are reduced to the same electrometer sensibility. The observations made on

TABLE VII.

*Second Sulphur Cylinder. April* 20, 1908.

| Speed. | (Speed)$^2$. | Deflection in cm. $\times$ 2. |
|---|---|---|
| 37.3 r.p.s. | 1391 | 0.70 |
| 70.5 " | 4970 | 3.09 |
| 96.9 " | 9390 | 5.70 |

earlier days were consistent with those given in the table, and many of them much better. The deflections given in the table are small for the reason that a stiff fiber was used while obtaining them.

The observations given in Table VII. are plotted in Fig. 16. The relation between the deflection and the square of the speed is seen to be linear. The deflections are far greater than those due to the effect which alone was expected.

The effect of heat on the non-magnetic effect was tried with a speed of 37 r.p.s. Two sets of observations were taken at the mean temperature 25° C., and between them a similar set at 41° C. The former gave the mean deflection 5.5, with an average departure from the mean of 0.3; while the latter gave the mean deflection 6.7, with an average departure from the mean of between 0.6 and 0.7.

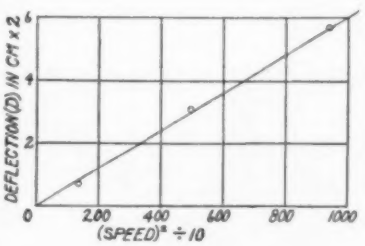

Fig. 16.

While the nature of the effect observed precluded the possibility of its being due to the presence of dust, it seemed worth while to try the effect of blowing the dust out of the region surrounding the rotor more thoroughly than had been done. This was done by a rotary blower, which sent a strong stream of air into and through the rotation chamber through a filter of cotton. But the effect persisted as before. The cylinder was finally destroyed to make room for the rosin cylinder described below.

The sulphur cylinder was cast on March 18, and the last experiments, given in the table, were performed on April 20. The experiments on the first sulphur cylinder were made nearly a year after the cylinder was cast and coated.

A few weeks after the completion of the experiments just de-

scribed another cylinder was cast, from roll sulphur, and was turned up and coated with paraffin and a very thin deposit of copper. The cylinder failed to insulate, however, and it was found that the acid had penetrated to the rotor through a small defect in the paraffin coat. Lack of time prevented further work on sulphur.

### LATER EXPERIMENTS WITH ROSIN.

Several attempts were made to cast and turn cylinders of brittle rosins, but without success. A cylinder was then prepared from rosin of the grade known as "extra water-white," which gave no difficulty in casting and turning. A much harder rosin could have been turned with ease. This cylinder was turned down to a mean diameter of 6.834 cm., the average departure from this mean of 17 readings properly spaced being less than 0.001 cm. This cylinder was coated with copper in the usual way. While the coat was very thin, the cylinder became slightly indented on one side, owing to its softness, but not sufficiently to injure it appreciably for the purposes of the experiments. The mean final external diameter of the copper coat was 6.912 cm. As the copper coat, after being treated with files and sand-paper, was not very uniform, 68 uniformly spaced readings of the diameter were taken. The average departure of a single measurement from the mean was 0.003 cm. The length of the copper cylinder was 33.6 cm., and that of the rosin a fraction of a mm. less, the ends of the rosin being made somewhat irregular by fusing them with a blow-pipe to prevent fine particles cracking off and flying away during the rotation experiments. The dielectric constant of the rosin for a charging time of $30^s$ was 3.22. The manner in which this constant varied with the time of charging, and also the manner in which the calibration deflection depended upon the time of charging and the interval elapsing between the end of the charging and the opening of key 3 are shown in the following table. The observations were made like the ordinary "calibration" observations, except that throws were taken instead of steady deflections.

The experiments on this rosin cylinder were performed under better conditions than those of 1907. Arrangements were made for heating the air within the key box and the tube connecting it

| Time. | Time of Charging. | Interval between Charging and Opening Key 3. | Mean Electrometer Throw. |
|---|---|---|---|
| $4^h\ 2^m$ | $30^s$ | $20^s$ | 5.21 |
| 12 | 30 | 40 | $5.22\frac{1}{2}$ |
| 21 | 30 | 20 | 5.20 |
| 34 | 5 | 20 | 5.13 |
| 40 | 20 | 20 | $5.18\frac{1}{2}$ |
| 48 | 40 | 20 | $5.20\frac{1}{2}$ |
| 57 | 30 | 20 | 5.19 |

with the electrometer box to a temperature considerably above the room temperature, and the insulation was further increased by inserting vessels of $CaCl_2$ in the boxes in addition to sulphuric acid. The room was not heated. Also, a rotary blower, already mentioned, was kindly placed at my disposal by my colleague Professor B. P. Caldwell. This blower was arranged to send a strong current of air into the region surrounding the rotor through two $CaCl_2$ bottles in series, one very large, the other smaller, and a thick layer of tight cotton wool. This removed dust very completely, and increased the insulation considerably. The blower was not kept going continuously, but was used from time to time. Also, as stated above, the direct current motor used in the earlier observations was replaced by an alternating current motor, whose speed, under the existing conditions, was much more nearly constant. The quartz fiber used in the electrometer was stiffer than that used in the earlier work, but the sensibility was entirely sufficient.

TABLE VIII.

*Second Rosin Cylinder. June* 8, 1908.

| No. of Set. | No. of Observations in Set. | $\tau \times 100$ in Seconds. | $I$ in Amperes. | $d$ in cm. $\times 2$. | $d/d_0$. | $d/d_0 \cdot V_0$ in Volts. | $d/d_0 \cdot V_0 \cdot \tau/I$. |
|---|---|---|---|---|---|---|---|
| 1 | 7 | 1.021 | 21.40 | 2.44 | 0.565 | 0.0556 | 0.0000265 |
| 2 | 10 | 1.021 | 11.42 | 1.274 | .296 | 292 | 261 |
| 3 | 8 | 1.016 | 11.72 | 1.36 | .319 | 314 | 272 |
| 4 | 8 | 1.020 | 20.74 | 2.38 | .565 | 557 | 274 |
| 5 | 7 | 1.772 | 20.16 | 1.28 | .306 | 301 | 265 |
| 6 | 10 | 1.769 | 10.96 | 0.673 | .162 | 159 | 257 |
| 7 | 8 | 1.019 | 18.74 | 2.03 | .490 | 483 | 262 |

Weighted mean 0.0000266

Average departure from mean 5

The results of the rotation observations made on June 8 are given in Table VIII., where the symbols have the same meanings as in earlier tables. Earlier observations, consistent with these but made before the best conditions were attained, were not reduced.

The method of observation was nearly identical with that used in the case of the first sulphur cylinder. The time elapsing between the opening of key 3 and the reading of the electrometer was shorter, owing to the quicker fiber and needle used.

Six determinations of the "calibration" deflection were made during the day. The average departure of a single determination from the value given by the curve was about 2 parts in 425.

From the data contained in Table VIII. and in what precedes, $\overline{U}$ is 0.00001618 volt + 0.00000075 volt = 0.0000169 volt; the mean value of $d/d_0 \cdot V_0 \cdot \tau/I - U$ is 0.0000097 volt; and the value of $\overline{W}\,(K-1)/K$ is $0.00001480 \times 2.22/3.22$ volt = 0.0000102 volt. Thus the discrepancy between the last two quantities, or the discrepancy between the experimental results and those called for by Lorentz's theory, is 5 parts in 102, or about 5 per cent., with an average departure from the mean of a trifle over 5 per cent.; while the discrepancy between the experimental results and those to be expected on the alternative theory is 51 parts in 148, over 34 per cent.

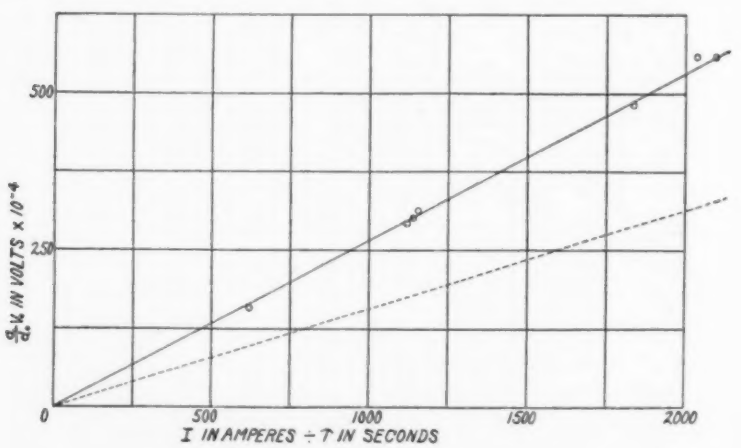

Fig. 17.

The experimental values of $d/d_0 \cdot V_0$ and $I/\tau$ are plotted in Fig. 17, the full straight line being drawn for the weighted mean. The

relation between the quantities is linear, as required by all theories. The dotted straight line shows the relation between $U$ and $I/\tau$.

### Later Experiments with Ebonite.

Rotor 1 had been slightly injured in preparing the first sulphur cylinder. It was therefore turned down slightly and electroplated with copper. The bearings were then turned down to the same diameter as before, and the central cylinder was turned to the diameter 5.106 cm., the mean of six readings about equally spaced along its length, the average departure from the mean being 0.001 cm. The ebonite cylinders used in the previous experiments were thoroughly cleaned, then heated considerably above the room temperature and forced onto the rotor hot, with thin layers of paraffin between them. The surface was then treated, in the lathe, with files and sand-paper until its mean diameter was 6.608 cm. The surface was not very true, the average departure from the mean of 32 properly spaced readings, in two planes, being 0.004 cm. The cylinder was then coated with copper by the process already described. The mean diameter of the copper coat, from 32 properly spaced measurements, was 6.711 cm., the average departure of a single measurement from the mean being 0.003 cm. It was found, however, that the cylinder failed to insulate, copper sulphate having penetrated some of the spaces between the separate ebonite cylinders. A similar failure of insulation resulted when V-shaped grooves, a few mm. deep, were cut into the junctions and filled carefully with hard shell-lac before electroplating. Finally, the grooves were cut out, rings of ebonite about 2.5 mm. thick being removed from the two cylinders at each junction, and the spaces were carefully filled with sealing wax. The surface was covered with a thin coat of Venice turpentine to make the carbon adhere better, and then electroplated as before. At first this cylinder insulated excellently, but later the insulation broke down. Two of the ceiling-wax rings were then cut out, and excellent insulation was found to be restored. Thin strips of metal were then soldered across the gaps to unite the different parts of the copper coat electrically. The total length of the ebonite and sealing-wax was now 32.5 cm., while the length of the central cylinder of the rotor was 33.6 cm. as before.

The capacity of the cylinder was determined as 297 E.S. units for $30^s$ as the time of charging. This gives as dielectric constant the enormous value 4.71, a straight-line field and a homogeneous dielectric being assumed as in the cases of the more nearly perfect cylinders. The capacity as determined was so great as to arouse strong suspicion that copper sulphate had penetrated between some of the ebonite cylinders from one of the armatures to within a small distance of the other. Hence, after the completion of the experiments described below, the remaining sealing-wax rings were cut out and the capacity was again determined, on two occasions. It had changed but slightly. As a further check, the capacity of the Leeds & Northrup condenser was again compared with that of the Elliott condenser, and was found to have remained unchanged. In the earlier experiments the dielectric constant of the same ebonite had been found to be 3.90. In these experiments the ebonite cylinders were on a rotor of diameter 5.044 cm., with little strain; while in the later experiments they were highly heated and shrunk onto a rotor of diameter 5.106 cm., so that they were under considerable strain when at normal temperature. They had, moreover, been heated several times in the interim.

TABLE IX.

*Ebonite Cylinder. June* 12, 1908.

| No. of Set. | No. of Observations in Set. | $\tau \times 100$ in Seconds. | $I$ in Amperes. | $d$ in cm. $\times 2$. | $d/d_0$. | $d/d_0 \cdot V_0$ in Volts. | $I/\tau$. | $d/d_0 \cdot V_0 \cdot \tau/I$. |
|---|---|---|---|---|---|---|---|---|
| 1 | 6 | 1.041 | 21.44 | 2.33 | 0.560 | 0.0551 | 2059 | 0.0000268 |
| 2 | 6 | 1.036 | 11.72 | 1.20 | .290 | 285 | 1131 | 252 |
| 3 | 6 | 1.785 | 20.74 | 1.25 | .310 | 305 | 1162 | 263 |
| 4 | 6 | 1.784 | 11.10 | 0.66 | .165 | 163 | 622 | 262 |
| 5 | 6 | 1.786 | 19.48 | 1.21 | .305 | 300 | 1091 | 275 |
| 6 | 7 | 1.048 | 10.88 | 1.12 | .284 | 279 | 1038 | 269 |

Weighted mean 0.00002654

Average departure from mean 0.0000006

The results of the rotation experiments, which were conducted very nearly like those upon the second rosin cylinder, with more use of the blower, are given in Table IX. During the observation day 4 sets of "calibration" deflections were obtained. The last set, as

well as the shortly preceding and last set of rotation experiments, was rejected for the reason that the insulation was becoming poor. The average departure of the deflections obtained from one of the calibration sets from the value given by the curve was about 1 part in 400.

The value of $\bar{\Psi}$, calculated on the assumption that the mean induction $\bar{B}$ was 88.65, as in the case of cylinders equal in length to the rotor, was 0.00001225 volt, and the value of $\bar{\Psi}(K-1)/K$ was 0.00000965 volt. The value of $\bar{U}$, calculated from the value of $\bar{U}$ for rotors 1 and 2, the difference between their radius and that of the rotor carrying the ebonite, and the mean induction $\bar{B}$ used above, together with the cross-section of the copper coat $F$, was 0.00001757 volt. The errors here introduced by the small departures from theo-

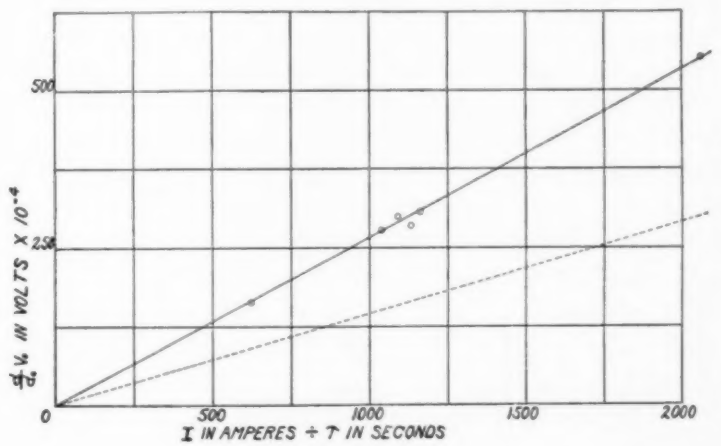


Fig. 18.

retical conditions are negligible in comparison with those introduced in the rotation experiments. The weighted mean value of $d/d_0 \cdot V_0 \cdot \tau/I$ was 0.00002654 volt. The difference between this quantity and $\bar{U}$ is 0.00000897 volt, which should equal 0.00000965 volt, the value of $\bar{\Psi}(K-1)/K$, on Lorentz's theory. The discrepancy is 7 per cent., with an average departure from the mean of the same magnitude. The discrepancy between the experimental results and those to be expected on the ether motion theory is 33 parts in 123, or 27 per cent.

The experimental results for $d/d_0 \cdot V_0$ and $I/\tau$ are plotted in Fig. 18. The full straight line is drawn for the weighted mean. The relation is linear, as with the other insulators. The dotted line gives the relation between $U$ and $I/\tau$.

The observations do not show the curious "centrifugal" effect described in connection with the first experiments on ebonite. In the later experiments the temperature of the ebonite was that of the tap-water, about 28° C.

### WILSON'S EXPERIMENTS.

The theory of Wilson's experiments, already referred to, can be developed without difficulty from equation (15) above.

Suppose the induction tube $G$ to be removed, the rod $JJ$ to be connected to the insulated quadrants of the electrometer, as well as to the insulated armature of a standard condenser, and the wire $N$ to be in permanent sliding contact with the metal tube $F$.

Let $S^{IV}$ denote the capacity of the tubes of displacement stretching between the conductor $F$ and the earthed conductors, the rotor being excepted; and $S^{V}$ the capacity of the tubes stretching between that part of the insulated system which is *always at rest*, viz., the wire $N$, the rod $JJ$, etc., and the earth. Let $V^{V}$ denote the potential of the insulated electrometer quadrants, which is equal to that of the wire $N$ and the part of the tube $F$ in contact therewith, when the rotor is in motion in the magnetic field. Then, in place of equation (15), we have

$$\Psi = V - U + \frac{S(V-U) + S^{IV}V + S^{V}V^{V}}{(K-1)S'''}. \qquad (26)$$

If we write $V^{V} - V = V^{IV}$, and eliminate $V$, this equation and (17) give

$$V^{V} = \frac{(K-1)S'''\Psi + S''(U + V^{IV}) + S^{IV}V^{IV}}{S'' + S^{IV} + S^{V}}. \qquad (27)$$

The electrometer gives a deflection $d$ proportional to $V^{V}$, by a constant $B$. Thus

$$V^{V} = Bd. \qquad (28)$$

If now the insulated system, *all* at rest, is given the charge $q_0$, it

will come to such a potential $V_0$, and the electrometer will give such a deflection $d_0$, that

$$V_0 = Bd_0 = \frac{q_0}{S'' + S^{IV} + S^{V}}. \tag{29}$$

From equations (27), (28), and (29), we obtain

$$q_0 \frac{d}{d_0} = [(K-1)S'''\Psi + S''(U + V^{IV}) + S^{IV}V^{IV}],$$

or

$$q_0 \frac{d}{d_0} = [(K-1)S'''\overline{\Psi} + S''(\overline{U} + \overline{V}^{IV}) + S^{IV}\overline{V}^{IV}]\frac{I}{\tau}, \tag{30}$$

which is the complete approximate formula for Wilson's experiments according to the theory of Lorentz. On the ether motion theory, $K-1$ must be replaced by $K$, the formulas derived from (26) by writing $K$ for $K-1$ and omitting $S(V-U)$, being

$$q_0 \frac{d}{d_0} = [KS'''(\overline{\Psi} + \overline{U} + \overline{V}^{IV}) + S^{IV}\overline{V}^{IV}]\frac{I}{\tau}. \tag{31}$$

In these experiments a contact piece, corresponding to the wire $N$, touched the metal coat of the rotating cylinder at its center. The rotor was covered with a thin insulating tube, and this was covered with a tube of brass. This tube was earthed near one end of the insulating cylinder under experiment, which it carried. This construction doubtless offered but little difficulty in the case of the small ebonite cylinder which alone was investigated by Wilson; but in such experiments as those described in this paper it would have introduced considerable difficulties. This construction gives a small value of $\overline{U}$; but in reducing $\overline{U}$ there is no advantage, as this quantity is easily determined with great precision.

The theory of his experiment, as given by Wilson with the assistance of Professor Larmor, is partially incorrect. Equation (30) may be written

$$q_0 \frac{d}{d_0}\frac{\tau}{I} - S''(\overline{U} + \overline{V}^{IV}) - S^{IV}\overline{V}^{IV} = \frac{K-1}{K}\cdot KS'''\overline{\Psi}. \tag{32}$$

Instead of the capacity $KS'''$ in the second member of this equation, Wilson has $S''$. His other terms correspond to those given in

the equation, although they are obtained in a very different way. Wilson's value of the first member of the equation is $12.74 \times 10^{-7}$ E.S. unit, while his value of the second member, with $S''$ incorrectly in place of $KS'''$ is $12.58 \times 10^{-7}$ E.S. unit, the discrepancy being about 1.3 per cent. In Wilson's work the value of $S''$ was 25.4 E.S. units and that of $KS'''$ was 24.3 E.S. units. If we correct the second member of (32), writing as above $KS'''$ instead of $S''$, its value becomes $12.04 \times 10^{-7}$ E.S. unit, which is nearly 6 per cent. less than the experimental value of the first member, viz., 12.74 E.S. units. On the ether motion theory, the second member must be replaced by $KS'''\mathfrak{V}$, which is $16.74 \times 10^{-7}$ E.S. unit. The discrepancy between Wilson's results and this theory is thus 4 parts in 16.7, or about 24 per cent.

Some time ago attention was called[1] by me to another error in Wilson's theory, which, however, did not affect his experimental work or calculations, but only the interpretation of his results. The electromotive force $\mathfrak{V}$ does not differ on the theory of Lorentz from its value on the ether motion theory, nor on either theory does it differ in conductors and insulators.

In the abstracts, already published, of a portion of this paper it was stated that in the third term of the second member of (30) Wilson had $S^{IV} + S^{V}$, and that neither of these quantities had been separately determined, which made it impossible to say what was the discrepancy between his results and those called for by the theory of Lorentz. This statement I deeply regret, as it is not correct. It was due to a curious and inexcusable misunderstanding of a line in Wilson's paper (l. 19, p. 135, l. c.).

A serious defect of Wilson's method lies in the insulated sliding contact with the inevitable abrasion and convection of charged particles from the brush and the coat of the rotating insulator. This defect can be eliminated by surrounding the rotating cylinder and brush with a second cylinder electrically connected with the brush

[1] Roy. Soc. Proceedings, 1905. This note was sent to the Royal Society by Lord Rayleigh at my request that this be done if he agreed with me that the note should be published in the Proceedings; but the technical communication was made by Professor Larmor, who wished to add a note in reply. To one who has read the two notes and the early part of the theoretical work in this paper, I do not think any further statement is necessary to justify my position.

and electrometer. The second cylinder should be longer than the first, as in the method described in this paper. In this case the modification would also eliminate any error due to friction between the initial coat of the insulating cylinder and dust in the air around it. For the algebraic sum of the charges developed at the contact or by friction with the dust is zero, and they would all be developed and retained within practically a closed hollow conductor. The same modification would also eliminate the term $S^{IV}V^{IV}$ from the formula.

## Conclusion.

The apparatus used in the investigation described in this paper could be modified in a few hours to operate by the method just suggested, and some experiments will possibly be made in this way next fall. In the fall I hope also to investigate a few cylinders by the method already used under still better conditions. The irregularities left in the case of the last experiments on rosin and ebonite are probably due in some way to imperfection of insulation, that of the insulating cylinder especially; and the insulation can be still further improved by making the apparatus much more nearly air tight. The insulation of a cylinder, after remaining in the bobbin all night with tap-water flowing through the jacket, may appear most excellent when tested with an electroscope after charging to a high voltage; and yet, unless great irregularities are to result, it must be much improved when the low voltage calibration and rotation experiments are to be performed. The trouble is not due principally to leakage of the low voltage charges normally produced in the course of the experiments, but to the charging up of the insulated conductors owing to the voltaic electromotive forces between them and the earthed conductors, which are many times greater than the normally developed electromotive forces to be measured. These effects are greatly reduced by improving the insulation, and are largely eliminated by the methods of observation used. Their practically complete elimination can doubtless be effected by the method suggested.

The curious electromotive force developed by the mere rotation of certain insulators I hope also to investigate further.

Nearly all of the apparatus built especially for this investigation

was constructed with great skill and patience by Mr. Tudor T. Hall, mechanician in this laboratory. To him I am also indebted for much other mechanical assistance, as well as for help in designing apparatus. A part of the instrumental work was skillfully done by the mechanicians, Messrs. Lange, Volz and Mann, of the laboratory of the National Bureau of Standards in Washington. In this laboratory, through the courtesy of Professor S. W. Stratton, Director of the Bureau, the apparatus was first set up, owing to the fact that power and other necessities were not available in my own laboratory in the summer of 1906. Although a severe illness of my assistant compelled me to desist from experimental work in Washington before I had fairly begun, I am much indebted for many kindnesses to Professor Stratton and his associates, who placed their splendid facilities freely at my disposal. The work has been completed with great difficulty, owing to exceptionally heavy pedagogical duties and other circumstances not necessary to mention here. Throughout the experimental work I have been assisted in the most faithful and efficient manner by Mrs. Barnett, to whom I am under further obligations for assistance in computing and for important suggestions.

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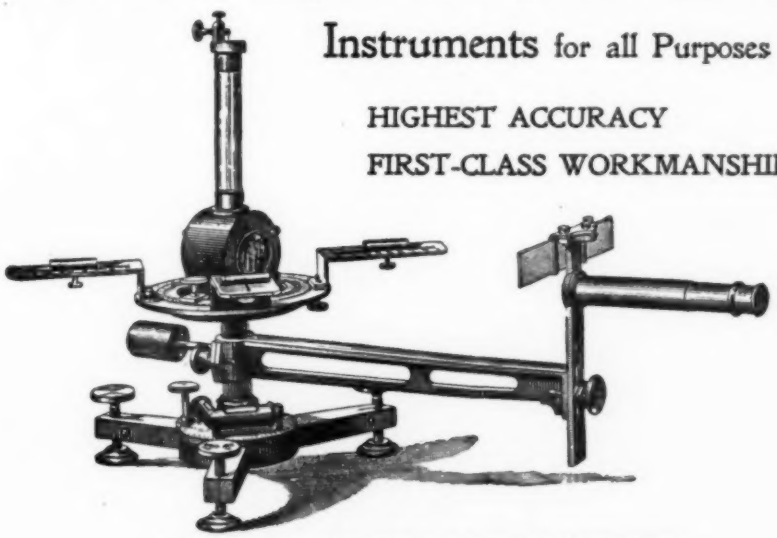

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